Studies in Analytical Chemistry and Electrochemistry with Particular Reference to Metallurgical Analysis

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To

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my teacher and friend

CONTENTS

ABSTRACT

The results of research in analytical chemistry and electrochemistry carried out in the University of Sheffield over a period of twenty four years are presented. The material consists of copies of fifty-five publications with an introductory section describing the research and the reasons for doing it. The publications are arranged into five sections namely (1) the use of hydrofluoric acid and fluorides in chemical analysis, (2) electrochemical investigations with emphasis on non-aqueous solvents, (3) atomic spectroscopic analysis with particular reference to the determination of trace elements in metals, (4) chemical phase analysis with emphasis on the quantitative determination of the types of nitrogen in steel and (5) miscellaneous publications.

Many of the publications, including at least one from each section, are concerned with the analysis of metals. Particularly noteworthy among these publications is the series of papers in section 3 on the determination of deleterious trace elements in steels, nickel-base alloys and copper using atomic absorption spectrometry with the introduction of solid samples to an induction furnace. This research spanning a period of twelve years has resulted in a fast, accurate and exceptionally sensitive method for the determination of volatile trace elements in metals.

DESCRIPTION AND RATIONALE OF THE RESEARCH

This thesis consists of 55 publications on original research and on works of scholarship such as reviews and a section of a book, which contain results not published in the author's research papers or which set in context a series of original publications from the author. These 55 publications are listed in Appendix 1, Section 6. Reviews and a second book written by the author and consisting mainly of appraisals of the work of others are not included in this thesis but are listed in Appendix 2.

Analytical chemistry or analytical science is a branch of applied chemistry and physics. Frequently in industrial and public laboratories the practice of analytical chemistry involves the determination of species through the application of well-tried methods or recipes. On the other hand, research in analytical chemistry is often concerned with the solution of analytical problems that occur in real life and for which no suitable methods are available. Then it is necessary to draw upon the vast store of scientific knowledge before engaging in new research in order to modify an existing method or to develop a new procedure. It is quite common for a research worker in analytical chemistry in an academic environment to try to apply a recent discovery or rediscovery in physical science to the determination of substances but he will be constantly aware that his research has little value if it does not result in analytical methods that are of interest to those who have to analyse samples from real life.

For this reason an academic staff member, who is an analytical chemist, should have good liaison with analytical chemists and others outside Universities to ensure that his research is relevant to some

of the needs of industry and the service activities such as quality assurance in government departments and forensic science and medicine, for which analysis is so essential. The ivory tower is a sterile place for the analytical chemist.

For the reasons just given the author has tried to maintain good contacts extramurally while he has carried out research over a period of 25 years along with his postgraduate students and associates in Sheffield University. At the beginning of this period, Sheffield was the centre of the special steel industry in the United Kingdom and is still very much involved with the production and fabrication of expensive steels. Therefore it was not surprising that the author soon became involved with steel analysts in the local works. The focal point for analysts was the British Iron and Steel Research Association, now part of the Sheffield Laboratories of the British Steel Corporation, where monthly meetings of the Analysis Group of the Sheffield Metallurgical and Engineering Association take place. It has been the good fortune of the author to know well and cooperate with first class analytical chemists on the local scene, men such as Mr. B. Bagshawe, late of Firth-Brown Ltd., Mr. G. M. Holmes, formerly of London Scandinavian and Metallurgical Co. Ltd. and Mr. P. H. Scholes of the British Steel Corporation. This cooperation resulted in research grants for equipment and research studentships for eight students. Also, of the 55 publications reproduced in this thesis, 31 resulted from work carried out in cooperation with the metallurgical industry. Most of the ideas for the research originated in the author's laboratory but without assistance from industry by way of money, equipment and materials, the research could not have been undertaken nearly so effectively. A list of the organisations to whom

the author is indebted is given in Appendix 3.

The publications have been classified into five sections as follows.

1. The use of hydrofluoric acid and fluorides in chemical analysis (Papers 1-13).
2. Electrochemical investigations with emphasis on non-aqueous solvents (Papers 14-23).
3. Atomic spectroscopic analysis with particular reference to the determination of trace elements in metals (Papers 24-44).
4. Chemical phase analysis with emphasis on the quantitative determination of the types of nitrogen in steel (Papers 45-50).
5. Miscellaneous publications (Papers 51-55).

Section 1. The use of hydrofluoric acid and fluorides in chemical analysis

Niobium, tantalum and tungsten were particularly troublesome elements to determine in solution before plastics unattacked by hydrofluoric acid became generally available in the 1950's. In this respect polyethylene, polypropylene and polytetrafluoroethylene are very useful. These early transition elements are difficult to retain in dilute solutions of hydrochloric, nitric and sulphuric acids but hydrofluoric acid forms very stable, soluble complexes with them. In 1959, the author in association with his early research students, began a series of studies into the application of hydrofluoric acid and fluorides in metallurgical analysis. It was his intention to develop completely reliable titrimetric methods for the determination of niobium and tungsten and to produce a suitable procedure for the separation of titanium, zirconium, niobium, tantalum, molybdenum and tungsten from each other and from other elements by the use of

ion-exchange resins, with the object of developing reliable and reasonably fast wet-chemical methods for the determination of these "difficult" elements in complex alloys, particularly steels. At that time, methods based on arc/spark emission spectroscopy and X-ray fluorescence spectroscopy had been developed for solid samples but they depended on the ready availability of analysed alloys for standardisation and reliable results for niobium, tantalum and tungsten could only be obtained wet-chemically after much careful and very tedious work. In 1959 investigations into the analytical applications of atomic absorption spectroscopy had just got under way in Australia and New Zealand, and the nitrous oxide-acetylene flame required for niobium, tantalum and tungsten was still to be discovered. (Its use was reported in 1965 [1]). Today inductively coupled plasma spectrophotometry is a very attractive technique for the determination of these elements in solution but the pioneering work of Reed on the inductively coupled argon plasma [2] had not yet taken place. By 1963 the hopes of the author had been realised and the results of these early investigations are described in Papers 1-5.

While studies were being undertaken on the redox reactions of niobium, molybdenum and tungsten in solutions containing hydrofluoric acid, it was noticed that trivalent ions are strongly complexed by fluoride but that monovalent and divalent ions are usually only weakly complexed (Paper 3). This results in iron(II) being a powerful reducing agent in fluoride media and in manganese(II) being quantitatively oxidised to manganese(III) by permanganate in the presence of fluoride. These observations were later applied to produce methods for the photometric titration of manganese(II) by permanganate in fluoride solutions with particular reference to the determination of manganese in alloys (Paper 6) and for the titrimetric

determination of quinones in fluoride solution with iron(II) (Paper 12).

In 1961-62 the author spent five months in the laboratories of Professor Louis Meites in Brooklyn Polytechnic, New York, studying electrochemical techniques. Professor Meites had recently written an excellent book on polarographic techniques [3]. On his return to Sheffield the author with his postgraduate students began to investigate the polarography of inorganic ions in fluoride media using the Teflon dropping mercury electrode developed by Raaen [4]. This led to four publications (Papers 7-10). Unfortunately titanium(IV), zirconium(IV), niobium(V), tantalum(V) and tungsten(VI) are reduced very irreversibly in fluoride media but good polarographic waves were obtained for molybdenum(VI) and several divalent ions (Paper 7). These investigations led to methods for the polarographic determination of molybdenum in niobium-base alloys (Paper 8), lead in a nickel-base alloy (Paper 9) and lead in steels after cation exchange separation (Paper 10).

Investigations on voltammetry of inorganic species in ammonium fluoride solution at a rotating platinum electrode are reported in Paper 11. An interesting wave for the oxidation of manganese(II) to manganese(IV) was discovered and the wave was employed to determine manganese in a series of steels of low cobalt content. These investigations using hydrofluoric acid and fluorides spanned a period of 10 years and, as a fitting end to this field of research, the author was pleased to review the research contributions from his group and those of others in an article entitled "The Application of Hydrofluoric Acid and Fluorides in Analytical Chemistry" (Paper 13). Looking back after ten years, the author feels that the most

satisfying work carried out in his laboratory with hydrofluoric acid and fluorides was concerned with the titrimetric determination of niobium and tungsten after reduction on columns of amalgamated zinc (Papers 3, 4 and 5). The reasons for non-quantitative reduction in all previous investigations were then obvious. By using hydrofluoric acid as a complexing agent to keep niobium, tantalum and tungsten in true solution, quantitative reduction was achieved and, by preventing subsequent reaction of the reduced species with hydrogen ion, titrimetric methods of high accuracy were developed.

Section 2. Electrochemical investigations with emphasis on non-aqueous solvents

Because of the disappointing results for the polarography of titanium(IV) and niobium(V) in fluoride media (Papers 7 and 9), the polarographic behaviour of these species and of molybdenum(VI) were reexamined in solutions of organic acids to see if a base electrolyte could be developed to enable them to be determined in complex alloys. A method was produced for the determination of molybdenum and titanium in a niobium-base alloy (Paper 14). However more than trace amounts of iron(III) and chromium(III) would have interfered with these determinations and it can be concluded that the polarographic techniques are not really suited for the determination of elements in complex alloys without time-consuming separation steps before electrochemical reduction. Therefore, it was not surprising that the author immediately terminated polarographic investigations on these early transition elements when the use of the nitrous oxide-acetylene flame in atomic absorption spectroscopy was reported in 1965 [1] (see Paper 25 in section 3).

In 1964, polarographic studies also commenced in acetic acid-

acetic anhydride solutions. This non-aqueous solvent was selected because aqueous solutions may be converted to this solvent mixture by adding the appropriate amount of acetic anhydride to the aqueous solution and refluxing until all water has been removed by reaction. Good polarographic waves were obtained for many ions, but, from an analytical point of view, there was little reason to select this non-aqueous solvent mixture rather than an aqueous solution (Paper 15). Most ions were reduced in the same order as in aqueous solution but it was noticeable that thallium(I) and several divalent cations were reduced at more positive potentials in 0.25 M acetous sodium perchlorate compared with 0.25 M aqueous sodium perchlorate. This greater ease of reduction is a result of the ions being less strongly solvated in acetic acid than in water and it prompted the author, in cooperation with his postgraduate research students, to investigate the polarographic behaviour of inorganic ions in sulpholan i.e. tetrahydrothiophene-1,1-dioxide (Paper 16), benzonitrile (Paper 17) and dimethylformamide (Paper 18), and of some inorganic oxyspecies in acetonitrile (Paper 19). There was much interest in electrochemical investigations of inorganic and organic compounds in non-aqueous solvents in the 1960's.

The author was particularly interested in the electrochemical behaviour of simple cations in non-aqueous solvents because polarographic investigations made in his laboratory and by others indicated that the inorganic cations in lower oxidation states should be stabilized to disproportionation in many non-aqueous solvents compared with water. This encouraged him to include a section on the electrochemical behaviour of simple cations in non-aqueous solvents in his book on electrochemical techniques for inorganic chemists [5] and this section is reproduced in this thesis as Paper 20. Results for

propylene carbonate and nitromethane not published in any previous papers are included in Table 13 on page 155. On page 159 comments are made concerning the stabilization of indium(I) in non-aqueous solvents of low coordinating ability and data on the stabilization of indium(I) in acetonitrile appear in Paper 21. Success in preparing solid compounds of indium(I) was finally achieved in the author's laboratory by reaction between indium amalgam and sub-stoicheiometric quantities of an appropriate silver(I) salt in acetonitrile (Paper 22). The author's suggestions made in Paper 20 for producing solutions of thulium(II) and neodymium(II) in a suitable non-aqueous solvent do not yet seem to have been taken up in another laboratory [6] and he hopes that he may get the opportunity to carry out further research on these systems in the future.

Section 3. Atomic spectroscopic analysis with particular reference to the determination of trace elements in metals

In the mid 1960's there was considerable discussion about the possibilities of developing new methods of steel production that would require the continuous analysis of molten steel [7]. The feasibility of analysing molten steel by spark emission spectrometry had not been adequately examined and the author along with Mr. A. K. Lambert, a postgraduate research student, studied the spectrographic determination of nickel in molten steel (Paper 24). It was shown that spark emission spectrometry is perfectly feasible for the analysis of molten steels. However, methods for the manufacture of steel, requiring continuous analysis through the production of sparks to liquid steel surfaces, have not yet materialised because of the difficult problem of readily obtaining a quiet liquid steel surface, which is slag-free.

Research into the use of atomic absorption spectroscopy in

metallurgical analysis commenced in the author's laboratory in 1965. The first paper to be published dealt with the determination of titanium in alloys using the nitrous oxide-acetylene flame (Paper 25). From 1967 until 1973, a series of investigations were undertaken into the determination of trace elements in steels using atomic absorption spectroscopy with financial support from the British Iron and Steel Research Association (Papers 26-32). Certain trace elements have detrimental effects on the mechanical properties of steels and their accurate determination is necessary in quality control. For concentrations in excess of 10-50 $\mu g\ g^{-1}$, depending on the element, arc emission spectrometry is the preferred method but standards analysed by atomic absorption spectrometry and sometimes molecular absorption spectrophotometry are required for the direct readers (arc/spark emission spectrographs with photomultiplier detection). Atomic absorption spectrometry is also employed if concentration levels below the limit of detection of the direct reader have to be determined.

Hollow cathode lamps are normally used as sources of atomic spectra for atomic absorption spectroscopy but in the late 1960's, the electrodeless discharge tube (or lamp) was developed as an alternative. The results of a comparison of these light sources for the determination of trace elements is published as Paper 26.

Studies on the determination of calcium, bismuth, antimony, tin, aluminium, and vanadium in steels were made and suitable procedures were developed. The results of these investigations are reported in Papers 27 to 32 respectively. For the determination of calcium in stainless steels, the major elements were removed by solvent extraction before concentration of the aqueous phase and its nebulization into a nitrous oxide-acetylene flame (Paper 27). The

methods developed and tested for the determination of trace concentrations of bismuth, antimony and tin in steels involved extraction of the trace element as an ion-association complex into 2-methyl-4-pentanone and concentration of the organic phase before introduction to the flame. For the determination of total aluminium in steel, treatment with acid in the normal way is ineffective in dissolving all of the aluminium oxide and the author and his postgraduate student resorted to a dissolution procedure involving a Teflon-lined pressure vessel. Complete solution was achieved in this way and trace levels of aluminium were determined by atomic absorption spectrometry after a procedure involving two solvent extractions.

Trace concentrations of vanadium in steel were also determined using atomic absorption spectrometry but, for this determination, the vanadium was separated from the major elements using a column of cation exchange resin before the effluent was concentrated for presentation to the flame (Paper 32).

Around 1970 these investigations were at the frontiers of development in metallurgical analysis, but research to produce new methods for the determination of trace elements goes on continuously and some of the elements mentioned above were soon to be determined more quickly and more conveniently by atomic absorption spectrometry coupled with furnace atomisation. Because of the high sensitivity of furnace methods, the solvent extraction step can be eliminated. For example, Frech has determined bismuth in steels using a furnace after a simple dissolution with a limit of detection of 0.5 $\mu g\ g^{-1}$ [8]. In a later publication (Paper 37), the author of this thesis describes how bismuth can be determined in steels by the addition of steel millings or turnings to a furnace for atomic absorption spectrometry with a limit of detection of 0.004 $\mu g\ g^{-1}$.

The series of papers on atomic absorption spectrometry after solvent extraction was terminated with an interesting study on the determination of iridium and ruthenium in rhodium sponge (Paper 33). This work involved dissolution of the rhodium in sealed glass tubes at 250°C and was carried out in cooperation with Johnson Matthey Chemicals Ltd.

In 1969 a series of investigations was begun into the determination of trace elements in metals by atomic absorption spectrometry after the introduction of solid samples into graphite induction furnaces designed and constructed in the author's laboratory. The first of these was a horizontal furnace, which was employed for the determination of cadmium in zinc-base metals (Paper 34). However its maximum temperature of operation was 1900°C and this was too low for the determination of many trace elements in steels. It was replaced with a vertical graphite induction furnace, which was employed for the determination of bismuth, aluminium, antimony and tin in iron-base alloys, bismuth in lead-base alloy, zinc in aluminium-silicon alloy and cadmium in zinc-base alloy (Papers 35 and 36). These investigations were continued with an improved vertical furnace and an atomic absorption spectrometer better suited for the research (a Perkin-Elmer 300S). Extensive investigations have been made into the determination of bismuth, silver, lead, and antimony and other elements in iron-base alloys (Papers 37 to 40 respectively), of bismuth, and silver and thallium in nickel-base alloys (Papers 41 and 42 respectively) and of bismuth, lead and tellurium in copper (Paper 43). This has been a most satisfying series of investigations. In the early 1970's, many analytical chemists said that furnace atomic absorption spectrometry with solid metal samples would not be suitable for quantitative determinations of volatile trace elements because of

homogeneity problems, but they have been proved wrong repeatedly. The method can scarcely be more straightforward and is extremely sensitive. This work is continuing with metals and glasses, but progress so far has been substantial and has been reviewed by the author (Paper 44). That paper compares and sets in context the work carried out by the author's group and others. So far only four groups have been active in this field, one in the U.S.A., two in Sweden and the author's, and it is to be hoped that the method will soon be more widely used.

The author is most grateful to the British Steel Corporation, Rolls-Royce Ltd., the Science Research Council and the Ministry of Defence for grants for equipment and materials during the last eight years to allow him to pursue the furnace work with solid samples, and to Rolls-Royce Ltd., Henry Wiggin and Co. Ltd., Ross and Catherall Ltd., BICC Metals Ltd., the British Cast Iron Research Association and the National Physical Laboratory for alloy samples and many useful discussions.

Section 4. Chemical phase analysis with emphasis on the quantitative determination of the types of nitrogen in steel

Progress in metallurgical analysis has been remarkable in the last forty years and the determination of any element in a metal at concentrations in excess of 10 $\mu g\ g^{-1}$ is now straightforward. Of course, efforts to develop faster and cheaper analytical methods for higher concentrations will continue to be pursued worldwide, but the difficult problems of 1940 have been solved. For specific metals and alloys, such as copper and nickel-base alloys, there is a need to determine some trace elements at concentrations less than 10 $\mu g\ g^{-1}$ and even as low as 0.02 $\mu g\ g^{-1}$ and this is still an active field of

research (see Section 3). No doubt, research will also be undertaken to determine even lower concentrations of trace elements in metals if there is a demand from the materials scientist for such analyses.

However, despite the successes in elemental analysis, many analytical problems remain to be solved in the field of phase analysis, or speciation in metals. The mechanical properties of metals usually depend on the presence of second phases and steels often contain oxides, nitrides and sulphides, in addition to carbides. These can be ternary as well as binary compounds. They also contain, at times, carbonitrides, oxynitrides, carbosulphides and oxysulphides. About 200 different types of inclusions or precipitates have been characterised in steels [9]. The quantitative determination of all the phases present in a steel can be a very demanding task and much work remains to be done in this field.

Second phases in metals are studied extensively by metallurgists using optical and electron microscopy but this work is associated more with identifying second phases and determining their size, shape and distribution than with determining their concentration. The Quantimet, which produces a magnified image of a selected surface area of a sample, is employed to count inclusions and to determine their percentage volume in the metal but the technique is only semiquantitative and lacks specificity. It can yield erroneous results in certain circumstances. A particle analysing scanning electron microscope using computer control (PASEM) has been developed recently and has been shown to produce quantitative results for the determination of certain non-metallic inclusions, such as sulphides, in steels [10, 11]. However it is not suited to the determination of carbon, nitrogen and oxygen, and few people could afford the luxury of a scanning electron microscope with EDAX attachment dedicated to this

type of work. Undoubtedly such physical methods for quantitative second phase determinations will be developed more extensively and, ultimately, may become the established methods for this type of work, but this is unlikely to be so until the 21st Century.

In the meantime, much remains to be done to improve existing methods and develop new methods for quantitative phase determinations using chemical procedures. The author has been involved in this type of work since 1973 and has received financial support for it from Steel Castings Research and Trade Association and the Science Research Council. A cell incorporating an ammonium ion-selective electrode was devised for the continuous monitoring of the release of mobile nitrogen from steel samples (Paper 45) and the extraction method with hydrogen was later modified for vanadium steels (Paper 46). The method has been extended to higher temperatures to allow the differentiation between and quantitative determination of more stable nitride phases in steels (Paper 47). Research for the last two publications was done in cooperation with Dr. S. R. Keown of the Department of Metallurgy at Sheffield University.

In the future it is hoped to determine mobile nitrogen and certain nitrides in steels by releasing dinitrogen into an argon gas stream as the steels dissolve in organic solvent-halogen mixtures. A preliminary investigation into the determination of very low levels of nitrogen in gas streams has been published (Paper 48) and this work is continuing. To assist in the selection of the most appropriate organic solvent-halogen mixtures for this type of work, studies have been undertaken to determine the solubilities of metals and of carbides, nitrides, oxides and sulphides, purchased as model compounds for inclusions in steels. The results of these studies appear in Papers 49 and 50. Investigations in this area are continuing in the

author's laboratory.

Section 5. Miscellaneous publications

Those publications which do not fit readily into the other sections are included here. The first of these is not a research paper but is concerned with the teaching of microchemistry in British Universities in 1961 (Paper 51). The information was collected from 32 chemistry departments of British Universities and analysed. During the last twenty years as more and more instrumental methods have been used in chemistry, the distinction between microanalysis, semi-microanalysis and macroanalysis has become blurred and it is now rather unrealistic to subdivide analytical methods in this way. For example, atomic absorption spectrometry is certainly a technique of microanalysis but it is also used to determine major elements in 1 g samples. The learning of special expertise to deal with microsamples is now much less necessary than it was forty years ago when so many methods were based on classical analysis. It is interesting to note that organised courses of lectures were seldom given to postgraduate students in our Universities in 1961. Of course, postgraduate lecture courses are now commonplace and many students, particularly in analytical chemistry, gain an M.Sc. degree as a result of course work and a short research dissertation.

Two short studies on the spectrophotometric determination of perrhenate and the complexometric titration of molybdenum(V) using photometric end-point detection are then reported (Papers 52 and 53). This work was done in the 1950's before the usefulness of atomic absorption and inductively coupled plasma spectrometry for these elements had been discovered.

Results for the determination of low concentrations of oxygen in

alloys using vacuum fusion followed by mass spectrometry are reported in Paper 54. This was work carried out in the laboratories of Firth-Brown Ltd. by Mr. E. D. Rawsthorne, a postgraduate student, under the supervision of Mr. B. Bagshawe, Chief Chemist, his staff and the author. The usefulness of a mass spectrometric finish for the determination of oxygen concentrations of less than 10 $\mu g\ g^{-1}$ is evident.

This section is terminated with a study on the differential spectrophotometric determination of molybdenum in ferromolybdenum (Paper 55). Differential spectrophotometry has been rather neglected as an analytical technique although it is well established that it is capable of yielding results of very good precision. Because the technique is not particularly selective, checks on its accuracy are essential, but for an appropriate system, excellent results can be achieved. A method of good accuracy and excellent precision was developed for the determination of molybdenum in ferromolybdenums of low copper and phosphorus contents.

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APPENDIX 1

THE PUBLICATIONS

Section 1. The use of hydrofluoric acid and fluorides in chemical analysis

The Analysis of Complex Alloys, with Particular Reference to Niobium, Tantalum and Tungsten

The Distribution of Metallic Ions between Ion-exchange Resins and Hydrochloric - Hydrofluoric Acid Solutions

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The distribution coefficients of aluminium, titanium^{IV}, zirconium, vanadium^{IV} and vanadium^{V}, niobium^{V}, tantalum, chromium^{III}, molybdenum^{VI}, tungsten^{VI}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and copper^{II} between the ion-exchange resins De-Acidite FF and Zeo-Karb 225 and up to 10 M hydrochloric acid (and mixtures 1 M in hydrofluoric acid and up to 10 M in hydrochloric acid) have been determined. From a study of the results, a scheme is proposed for the separation of these elements into more manageable groups.

The wet-chemical quantitative determination of niobium, tantalum and tungsten in complex alloys has always been a lengthy procedure, partly owing to the ease with which salts of these metals are hydrolysed in acid solution and partly because of the similarity between their chemical properties. In the procedure often used, niobium and tantalum are completely precipitated as their hydrated oxides; most of the tungsten is co-precipitated as tungstic acid,[1,2] and the remainder is removed from the solution as its insoluble complex with rhodamine B.[1] In this way, these elements can be separated from most of the other constituents of the alloy. However, clean-cut separation is difficult to achieve, and the ignited precipitate usually contains almost all of the silicon and small amounts of certain other oxides, such as titanium dioxide and molybdenum trioxide. Silicon can be readily removed by treatment with hydrofluoric and sulphuric acids, but the presence of small amounts of the other oxides must be allowed for in the subsequent analysis of the ignited precipitate for niobium, tantalum and tungsten. Satisfactory analysis of this ignited precipitate usually necessitates further separation into individual constituents. Niobium and tantalum can be separated from tungsten by fusion of the oxides in potassium carbonate and precipitation of the niobium and tantalum by magnesium sulphate and ammonium chloride,[2,3] but the separation of niobium from tantalum by precipitation reactions has, until recently, been time-consuming. These elements can be more readily separated on columns of cellulose[4] or ion-exchange resins[5] or by solvent extraction.[6,7] (Recently, however, the use of *N*-benzoyl-*N*-phenylhydroxylamine for precipitating niobium, tantalum and titanium substantially free from almost all other elements, including tungsten, and for the separation by consecutive precipitation under different conditions of niobium, tantalum and titanium has been described[8,9]; this technique appears to show promise, but no results seem to have been published for the determination of niobium and tantalum in complex alloys by means of this reagent.)

The combination of precipitation and separation does, however, after many hours' work, produce the correct results for the niobium, tantalum and tungsten contents of an alloy. For example, Hague and Machlan[10] have satisfactorily determined niobium, tantalum, titanium and zirconium (but not tungsten) in steels by precipitating these elements from solution with cupferron, igniting the precipitate to give the mixed oxides and separating the constituents of the solution of mixed oxides on a column of ion-exchange resin.

The time taken for an analysis would be greatly decreased if its first stage, the precipitation of niobium, tantalum and tungsten, could be by-passed, and we decided to examine the possibility of analysing alloys containing niobium and tantalum or niobium, tantalum and tungsten entirely by the use of ion-exchange resins. These elements only remain dissolved in dilute acid in the presence of certain complexing agents, and solutions of hydrofluoric acid in hydrochloric acid were used for this purpose. Wilkins[11] has described the separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium and tantalum by a method not involving initial precipitation and in which fluoride

solutions and ion-exchange resins were used; so far, however, no results for the application of his scheme to alloys containing widely different amounts of these elements have been published. Wetlesen[12] has also reported a satisfactory method for the analysis of mixtures of titanium, niobium and tantalum; he used hydrochloric - hydrofluoric acid solutions and a column of the anion-exchange resin Amberlite IRA-400, but did not examine the effects of other metals on the separation.

So that the desired separations might be achieved in a reasonable time, we have used resins of mesh size 52 to 100; much work on ion-exchange separation has been carried out by American investigators with 200-mesh resin, but it was thought that the rate of flow through resin of this size would be too slow for our purposes. The resins chosen for this work were De-Acidite FF (type SRA 70) and Zeo-Karb 225 (type SRC 14), obtainable from the Permutit Co. Ltd., London. In order to devise the best possible scheme for solutions of alloys, it was necessary to determine the distribution coefficients of niobium, tantalum, tungsten, etc., between the hydrochloric - hydrofluoric acid solutions and the cation- and anion-exchange resins; in this paper, the results of these studies are reported.

Values of distribution coefficients can be applied directly to work on columns by means of the following equation[13]—

$$V_{max.} = D_v + i$$

provided that the total amount of cation or anion is less than about 3 per cent. of the total capacity of the column.[14] In this equation, $V_{max.}$ is the volume (in column volumes) eluted when the maximum concentration of metal ion is observed in the effluent, D_v is the volume-distribution coefficient of the element between the resin and the solution and i, a fraction, is the interstitial volume of the column of resin. The value of D_v is found by batch-equilibration experiments and is defined by the expression—

$$\frac{\text{Amount of element on resin/volume of resin (in litres)}}{\text{Amount of element in solution/volume of solution (in litres)}}.$$

The value of D_v varies with the loading of the resin, decreasing as the loading increases, but generally does not alter appreciably for loadings less than 3 per cent. of the total capacity. Since, in subsequent work with columns, we intended to keep the total column loading to less than 3 per cent. for ions appreciably adsorbed, it was thought that the values of D_v found with a resin loading of never more than 3 per cent. could be used with reasonable exactness to predict the positions of band maxima in elution studies.

Kraus and his co-workers have determined distribution coefficients for most metals between the anion-exchange resin Dowex 1-X10 (*i.e.*, Dowex 1 containing 10 per cent. of divinylbenzene) of 170 to 220 mesh and hydrochloric acid[15] and hydrochloric - hydrofluoric acid media.[16] However, their results for niobium, tantalum and zirconium refer to 0·5 M hydrofluoric acid with different concentrations of hydrochloric acid, and our investigation was made entirely with 1 M hydrofluoric acid and different concentrations of hydrochloric acid. The resin De-Acidite FF was also expected to show some difference in affinities for certain elements when compared with Dowex 1 under the same experimental conditions. Recently,[17] distribution coefficients have been determined for some fifty elements between 200-mesh Dowex 1-X10 resin and pure hydrofluoric acid solutions. That work indicated, however, that hydrofluoric acid was less versatile a reagent than hydrochloric - hydrofluoric acid mixture.

The distribution coefficients of many elements between the cation-exchange resin Zeo-Karb 225 and hydrochloric - hydrofluoric acid media are also reported in this paper. Little work has so far been carried out on distribution coefficients with cation-exchange resins. Strelow[18] determined the distribution coefficients of forty-three cations between 100- to 200-mesh AG50W-X8 resin (prepared from Dowex 50) and hydrochloric acid, but he used rather a high column loading (40 per cent.). Mann and Swanson[19] have also recently determined the distribution coefficients of manganese, iron^{II}, iron^{III}, nickel, copper^{II}, zinc, cadmium and mercury^{II} between 0·5 to 12 M hydrochloric acid and 100- to 200-mesh Dowex 50W resin containing 2, 4, 8, 12 or 16 per cent. of divinylbenzene.

In our work, it was more convenient to determine weight-distribution coefficients for elements between the solutions and resins, but these can be readily converted to volume-distribution coefficients by means of the relationship—

$$D_v = D\rho$$

in which D is the weight-distribution coefficient and ρ is the density of the resin bed in kilograms per litre (the value of ρ is 0·41 for De-Acidite FF resin, type SRA 70, and 0·43 for Zeo-Karb 225 resin, type SRC 14). The weight-distribution coefficient is given by the expression—

$$\frac{\text{Amount of element on resin/weight of resin (in kilograms)}}{\text{Amount of element in solution/volume of solution (in litres)}}.$$

In determining weight-distribution coefficients by batch-equilibration experiments, it was convenient to shake a few grams of resin with a few millilitres of solution in small polythene bottles. Distribution coefficients were calculated from the final concentration of an element in the solution and from the decrease in concentration of the solution after it had been shaken with the resin. As the total resin loading was at no time to exceed 3 per cent., solutions containing metals in low concentration had to be used, and the concentrations of elements in the solution before and after being shaken with the resin were determined by sensitive colorimetric procedures.

Experimental

Apparatus—

Polythene ware—For determining distribution coefficients, solutions and resins were shaken in polythene 1-oz bottles fitted with polythene screw-caps. Solutions containing hydrofluoric acid were kept in polythene bottles and vessels.

Shaker—A mechanical shaker was constructed to accommodate twelve polythene bottles. The speed of shaking could be altered by means of a rheostat, but the motor on the shaker was generally operated at about 500 cycles per minute.

Spectrophotometer—A Unicam SP600 instrument was used in the colorimetric determinations of metals in solution.

pH meter—A Pye universal pH meter was used when necessary.

Resins—

Zeo-Karb 225—Type SRC 14 was used; it contained 8 per cent. of divinylbenzene and consisted of particles of size between 52 and 100 mesh. Before use, the resin was thoroughly washed in a column, first with 2 N hydrochloric acid to convert it from the sodium form (as supplied) into the hydrogen form and then with distilled water until the effluent was free from chloride. Finally, it was dried over anhydrone *in vacuo* at 60° C.

De-Acidite FF—Type SRA 70 was used; its cross-linking was approximately 7 to 9 per cent., and it consisted of particles of size between 52 and 100 mesh. It was supplied in the chloride form, but, before use, was treated with hydrochloric acid and washed and dried as described above for Zeo-Karb 225.

Standard solutions of metals—

These were prepared from Specpure metals or oxides obtained from Johnson, Matthey and Co. Ltd.

For work with hydrochloric - hydrofluoric acid solutions—Standard solutions of aluminium, titanium^{IV}, zirconium, vanadium^{V}, niobium^{V}, tantalum, chromium^{III}, molybdenum^{VI}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and cerium^{IV} were prepared by dissolving in 40 per cent. w/w hydrofluoric acid, with heating when necessary, weighed amounts of the following materials: aluminium rod, titanium sponge, zirconium oxide, vanadium pentoxide, niobium pentoxide, tantalum pentoxide, chromium pellets, molybdenum trioxide, manganese flake, iron sponge, cobalt sponge, nickel sponge and ceric oxide. Iron and titanium sponge dissolved in the hydrofluoric acid with the formation of iron^{II} and titanium^{III}, respectively. Iron^{II} was oxidised to iron^{III} by hydrogen peroxide, excess of which was destroyed by boiling. Titanium^{III} was oxidised to titanium^{IV} by adding concentrated nitric acid dropwise to the boiling solution.

A standard solution of copper^{II} was prepared by dissolving powdered copper in the hydrofluoric acid, with the addition of hydrogen peroxide; excess of hydrogen peroxide was destroyed by boiling.

A standard solution of tungsten^{VI} was prepared by dissolving tungsten trioxide in ammonia solution, sp.gr. 0·880, evaporating the solution to dryness and dissolving the residue in the hydrofluoric acid.

The concentration of residual hydrofluoric acid in these solutions was adjusted to about 5 M and accurately determined by titration with standard alkali. The concentrations of metals in the solutions varied from 0·4 to 4 mg per g.

Standard vanadium^{IV} solution was prepared by bubbling sulphur dioxide for 15 minutes through a solution of vanadium pentoxide (about 50 mg) in 50 ml of 10 M hydrofluoric acid, removing the excess of sulphur dioxide by boiling and then diluting with water until the concentration of vanadium^{IV} was approximately 0·5 mg per g.

For the solution of cerium^{IV}, the metal content was determined by adding a suitable volume of standard iron^{II} solution to an aliquot of the cerium^{IV} solution and then determining the excess of iron^{II} colorimetrically with bipyridyl[20]; this was necessary because it could not be assumed that Specpure ceric oxide contained 100 per cent. of CeO_2.

For work with hydrochloric acid containing no hydrofluoric acid—Standard solutions of aluminium, vanadium^{V}, chromium^{III}, manganese^{II}, iron^{III}, cobalt^{II} and nickel were prepared by dissolving about 100 mg of the Specpure metal or oxide in 10 to 20 ml of water containing the minimum amount of concentrated hydrochloric acid and diluting with water until the concentration of metal was approximately 1 mg per g. With iron^{III}, hydrogen peroxide was added to the solution to oxidise iron^{II}, and the excess of peroxide was destroyed by boiling.

A standard solution of copper^{II} was prepared by dissolving powdered copper in the minimum volume of a mixture of hydrochloric acid and 30 per cent. w/v hydrogen peroxide solution, destroying the excess of peroxide by boiling and diluting with water until the concentration of copper^{II} was about 1 mg per g.

Residual hydrochloric acid in these solutions was determined by titration with standard alkali.

OTHER REAGENTS—

Hydrochloric, hydrofluoric and sulphuric acids—These were of analytical-reagent grade.

Reagents and solutions for colorimetric determinations—These were of the purest grade available.

DETERMINATION OF DISTRIBUTION COEFFICIENTS

PROCEDURE FOR ZEO-KARB 225 OR DE-ACIDITE FF AND HYDROCHLORIC - HYDROFLUORIC ACID SOLUTIONS—

An aliquot (1 to 2 ml) of the standard solution of the metal in hydrofluoric acid was placed in a tared 1-oz polythene bottle and accurately weighed; from the density of the solution, the exact volume of the aliquot was determined. Calculated volumes of concentrated hydrochloric acid and water were then added from burettes to adjust the concentration of hydrofluoric acid to 1 M and that of hydrochloric acid to the required value. The bottle and its contents were then weighed to ascertain the total weight of solution. A 0·5- to 1·0-g portion of dried resin was placed in the bottle, and the exact amount used was found by weighing the bottle and contents; this amount was such as to give a total resin loading of less than 3 per cent. The bottle, together with eleven others containing resin and solutions having different ratios of hydrochloric to hydrofluoric acid, but prepared in a similar way, was shaken mechanically for a minimum of 16 hours. (With Zeo-Karb 225 and solutions 7 M or more in hydrochloric acid, the time of shaking was only 30 minutes, as the resin was slowly attacked by the acid at these concentrations.)

Some of the hydrochloric - hydrofluoric acid solution was then filtered through a dry 5·5-cm Whatman No. 42 filter-paper supported in a 1½-inch polythene funnel, collected in a weighed tall 100-ml beaker and weighed. The concentration of residual metal in the solution was determined by one of the methods outlined below.

PROCEDURE FOR ZEO-KARB 225 OR DE-ACIDITE FF AND HYDROCHLORIC ACID—

The procedure was similar to that described above, but the aliquot of filtered solution was collected in a small calibrated flask before being weighed.

TREATMENT OF SOLUTIONS BEFORE COLORIMETRIC DETERMINATION—

As most of the colorimetric determinations were carried out in acid solution, it was necessary to remove hydrofluoric acid from the weighed aliquots of hydrochloric - hydrofluoric acid solutions to prevent the glass cells from being attacked. If it was known that the colorimetric method was subject to no interference from the presence in the solution of

silicon, boron or aluminium, 2 ml of concentrated sulphuric acid were added to each hydrochloric - hydrofluoric acid solution, and the mixture was evaporated in a Pyrex-glass beaker until fumes of sulphur trioxide were evolved. When interference from silicon, boron or aluminium was expected, concentrated hydrochloric acid was added, and the solution was evaporated to dryness in a polytetrafluoroethylene beaker; this evaporation served to free the solution from hydrofluoric acid. With weighed aliquots of solutions containing only hydrochloric acid, evaporation with concentrated sulphuric acid was not necessary.

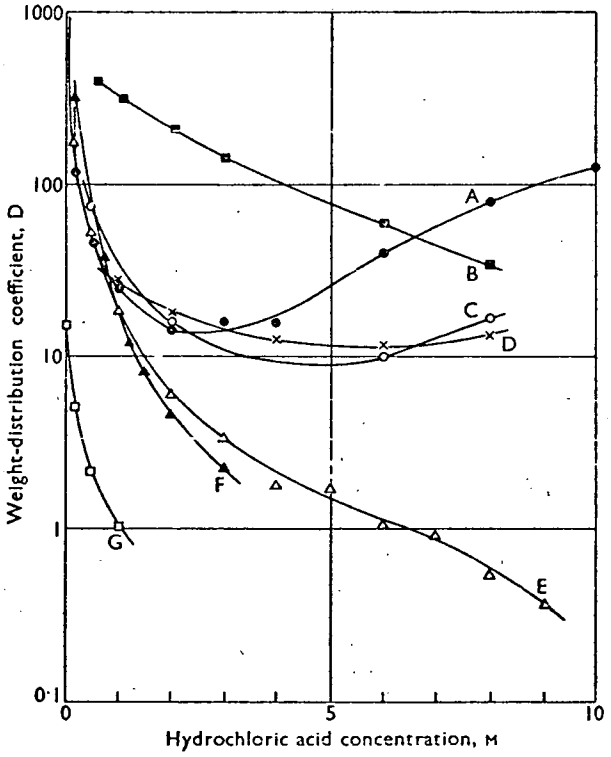

Fig. 1. Weight-distribution curves between De-Acidite FF resin and solutions 1M in hydrofluoric acid and containing different concentrations of hydrochloric acid: curve A, molybdenum^{VI}; curve B, tantalum; curve C, niobium^{V}; curve D, tungsten^{VI}; curve E, titanium^{IV}; curve F, zirconium; curve G, vanadium^{V}

COLORIMETRIC DETERMINATIONS OF METALS—

The concentrations of metal ions in the solutions were determined as outlined below, all or only part of the solution being used, depending on the amount of metal present and the sensitivity of the colorimetric procedure.

Aluminium—This was determined as its complex with Solochrome cyanine R in a solution buffered at pH 6·0 with pyridine and hydrochloric acid; optical-density measurements were made at 537 mμ.[21]

Titanium^{IV}—This was determined as its complex with chromotropic acid in a solution buffered at pH 4·0 with acetic acid and sodium acetate; optical-density measurements were made at 438 mμ.[22]

Zirconium—This was determined as its complex with xylenol orange in 0·2 N sulphuric acid; optical-density measurements were made at 535 mμ.[23]

Vanadium—Vanadium^{IV} was determined as its complex with catechol in ammoniacal solution (pH 8 to 9),[24] and vanadium^{V}, after reduction by sulphite,[24] was similarly determined; optical-density measurements were made at 585 mμ.

Niobium^{V}—This was determined by extraction into ether of its complex with potassium thiocyanate and subsequent measurement of optical density at 385 mμ.[25]

Tantalum—This was determined with pyrogallol, optical-density measurements being made at 365 mμ.[26]

Chromium^{III}—This, after oxidation to the sexavalent state, was determined as its complex with diphenylcarbazide in a dilute solution of orthophosphoric acid; optical-density measurements were made at 540 mμ.[27]

Molybdenum^{VI}—This was determined as its complex with toluene-3,4-dithiol in an aqueous solution containing 30 per cent. v/v of butyl alcohol and 5 M in hydrochloric acid; optical-density measurements were made at 680 mμ.[28]

Tungsten^{VI}—This was determined after extraction of its complex with toluene-3,4-dithiol into carbon tetrachloride; optical-density measurements were made at 635 mμ.[29]

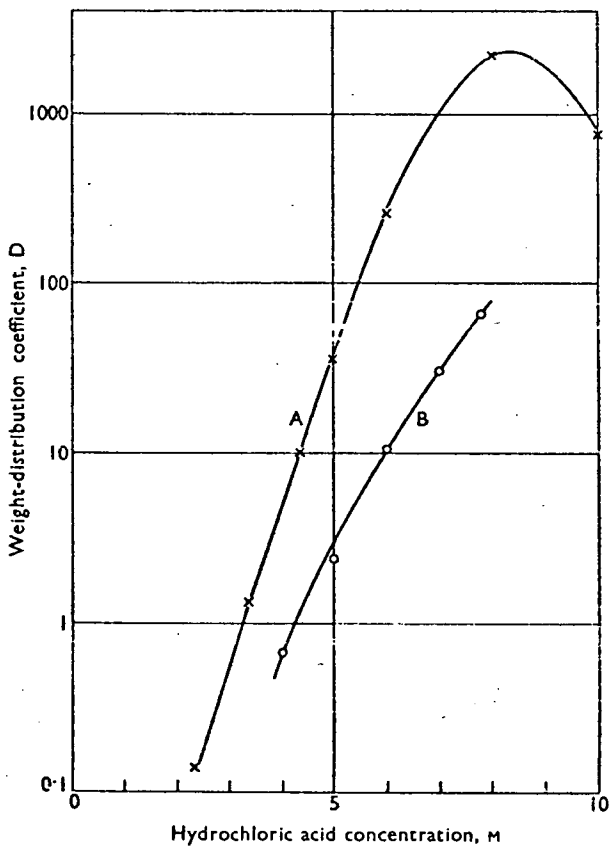

Fig. 2. Weight-distribution curves for iron and cobalt (conditions as in Fig. 1): curve A, iron^{III}; curve B, cobalt^{II}

Manganese^{II}—This was determined, after oxidation by periodate, as permanganate, optical-density measurements being made at 525 mμ.[30]

Iron^{III}—This was determined, after reduction by hydroxylamine, as its complex with bipyridyl; optical-density measurements were made at 522 mμ.[20]

Cobalt^{II}—This was determined as its complex with nitroso-R salt, optical-density measurements being made at 530 mμ.[31]

Nickel—This was determined as its complex with dimethylglyoxime, after oxidation by bromine; optical-density measurements were made at 465 mμ.[32]

Copper^{II}—This was determined by extraction into carbon tetrachloride of its complex with sodium diethyldithiocarbamate, optical-density measurements being made at 435 mμ.[33]

Cerium^{IV}—This was determined by adding an excess of standard iron^{II} solution and then determining the unreacted iron with bipyridyl, optical-density measurements being made at 522 mμ.[20]

Results for De-Acidite FF resin

Fig. 1 shows graphs of weight-distribution coefficient, D, against concentration of hydrochloric acid for titanium^{IV}, zirconium, vanadium^{V}, niobium^{V}, tantalum, molybdenum^{VI} and tungsten^{VI} in solutions 1 M in hydrofluoric acid; D is plotted on a logarithmic scale. Similar graphs for iron^{III} and cobalt^{II} are shown in Fig. 2, and individual results for a few other elements are listed in Table I.

Table I

Weight-distribution coefficients for various elements on De-Acidite FF resin

Element	Solution	Value of D
Aluminium	Hydrochloric acid, 8 M	<0·5
Vanadium^{IV}		1·5
Chromium^{III}		<0·5
Nickel		<0·5
Aluminium	Hydrofluoric acid, 1 M	<0·5
Vanadium^{IV}		0·7
Chromium^{III}		<0·5

The distribution coefficients for manganese^{II}, iron^{III} and copper^{II} between the resin and hydrochloric acid are shown in Fig. 3.

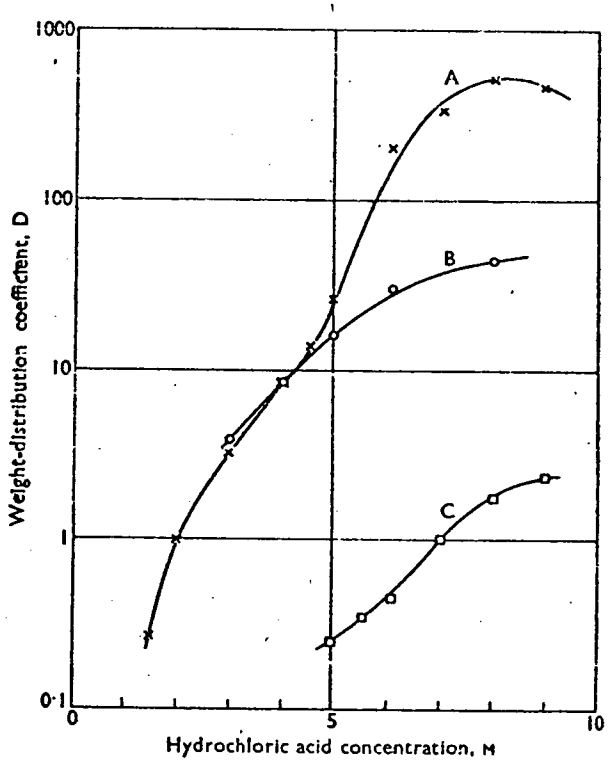

Fig. 3. Weight-distribution curves between De-Acidite FF resin and hydrochloric acid: curve A, iron^{III}; curve B, copper^{II}; curve C, manganese^{II}

Results for Zeo-Karb 225 resin

Fig. 4 shows graphs of weight-distribution coefficient against concentration of hydrochloric acid for vanadium^{IV}, chromium^{III}, iron^{III} and cobalt^{II} in solutions 1 M in hydrofluoric

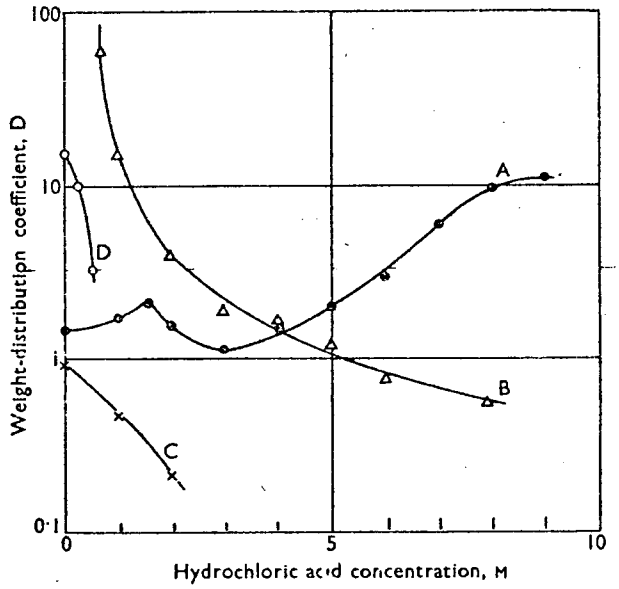

Fig. 4. Weight-distribution curves between Zeo-Karb 225 resin and solutions 1 M in hydrofluoric acid and containing different concentrations of hydrochloric acid: curve A, iron^{III}; curve B, cobalt^{II}; curve C, chromium^{III}; curve D, vanadium^{IV}

acid. Similar graphs for solutions containing no hydrofluoric acid are shown in Fig. 5 for aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, iron^{III}, nickel and copper^{II}. Other results for some of these elements are listed in Table II.

TABLE II

WEIGHT-DISTRIBUTION COEFFICIENTS FOR VARIOUS ELEMENTS ON ZEO-KARB 225 RESIN

Element	Solution	Value of D
Aluminium	Hydrochloric acid (0 to 1 M) - hydrofluoric acid (1 M)	<0·5
Vanadium^{V}	Hydrofluoric acid, 1 M	1·2
	Hydrochloric acid, 0·06 M	32
Manganese^{II}	Hydrofluoric acid, 1 M	>2000
Nickel	Hydrochloric acid (0·1 M) - hydrofluoric acid (1 M)	~5000
Copper^{II}	Hydrofluoric acid, 1 M	>7000

DISCUSSION OF RESULTS

DE-ACIDITE FF RESIN—

As expected, the curves in Fig. 1 for titanium^{IV}, zirconium, niobium^{V}, tantalum, molybdenum^{VI} and tungsten^{VI} were similar in shape to those obtained by Nelson, Rush and Kraus,[16] who used the anion-exchange resin Dowex 1. At low concentrations of hydrochloric acid, these elements are strongly adsorbed on the resin, as they form fairly stable anionic complex fluorides that compete favourably with chloride ions for sites on the resin. Nelson, Rush and Kraus[16] did not study the adsorption of vanadium^{V} in detail, but it is evident from Fig. 1 that this element is appreciably adsorbed at low concentrations of hydrochloric acid. Vanadium^{V} is not particularly stable in the presence of De-Acidite FF; in fact, it was rapidly reduced to vanadium^{IV} in the presence of 10 M hydrochloric acid. In 5 M hydrochloric acid, a determination of the ratio of vanadium^{V} to vanadium^{IV} after being shaken for 30 minutes with the resin showed that 67 per cent. of the vanadium^{V} had been reduced. At concentrations of hydrochloric acid less than 1 M, reduction of vanadium^{V} appears to be negligible, and the values of D for vanadium^{V} in solutions 1 M in hydrofluoric acid and up to 1 M in hydrochloric acid are considered to be reliable. However, the concentration of

acid at which reduction begins is not known exactly, and no other values of D are therefore reported for vanadium^{V}.

The curves in Fig. 2 for iron^{III} and cobalt^{II} are also similar in shape to those obtained by Kraus and his co-workers,[15,16] although they determined the distribution coefficients for cobalt^{II} with only hydrochloric acid (up to 10 M). However, the curves obtained in presence and absence of 1 M hydrofluoric acid will be similar in shape, as cobalt^{II} does not form anionic complexes with fluoride.[34] Likewise, manganese^{II}[34] and copper^{II}[35] show no tendency to form anionic fluoride complexes; graphs for these elements (Fig. 3) were plotted from the results obtained with hydrochloric acid alone instead of mixed with hydrofluoric acid, as results could more speedily be obtained with the former solution. The presence of 1 M hydrofluoric acid will have little or no effect on these curves.

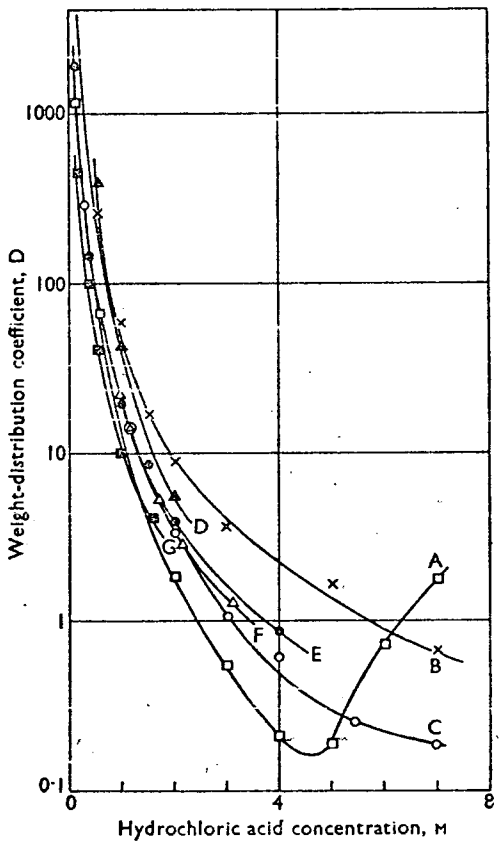

Fig. 5. Weight-distribution curves between Zeo-Karb 225 resin and hydrochloric acid: curve A, iron^{III}; curve B, chromium^{III}; curve C, manganese^{II}; curve D, aluminium; curve E, copper^{II}; curve F, nickel; curve G, vanadium^{IV}

Aluminium, vanadium^{IV}, chromium^{III} and nickel are adsorbed either not at all or only slightly on Dowex 1 from hydrochloric acid of any concentration.[15] If they were to be adsorbed on De-Acidite FF from hydrochloric acid, adsorption would occur only at high concentrations of acid; however, the results in Table I show that there was little or no adsorption of these elements from solutions 8 M in this acid. If aluminium, vanadium^{IV} and chromium^{III} were to be appreciably adsorbed from hydrochloric - hydrofluoric acid solution, such adsorption could occur only at low concentrations of hydrochloric acid, when any anionic fluoride complexes formed could compete favourably with a low concentration of chloride ions for sites on the resin. However, it is evident from Table I that neither aluminium nor chromium^{III} is adsorbed on De-Acidite FF from 1 M hydrofluoric acid and that vanadium^{IV} is adsorbed only slightly.

The distribution coefficients of cerium^{IV} between De-Acidite FF and hydrochloric - hydrofluoric acid solution could not be determined, as, in presence of the resin, cerium^{IV} was rapidly reduced to cerium^{III}.

With solutions containing only hydrofluoric acid (1 M), it could not be assumed that the solution, after being shaken with the resin, contained no chloride ions. However, strongly basic anion-exchange resins have much greater affinity for chloride than for fluoride,[36] and, as the concentration of fluoride as F^- and HF_2^- in 1 M hydrofluoric acid is approximately 0·06 gram-ion per litre, it seemed likely that the concentration of chloride ions would not exceed 0·1 M and would probably be very much less. In an experiment in which 1 g of dry resin was shaken with 5 ml of 1 M hydrofluoric acid, the concentration of chloride ions in the solution after the shaking was 0·015 M.

ZEO-KARB 225 RESIN—

The curves in Fig. 4 for vanadium^{IV}, chromium^{III} and iron^{III} and the values of D for aluminium in Table II indicate that all of these elements are appreciably complexed with fluoride at low concentrations of hydrochloric acid. Aluminium, chromium^{III} and iron^{III} are scarcely adsorbed on Zeo-Karb 225 in presence of 1 M hydrofluoric acid and at concentrations of hydrochloric acid less than 5 M, and vanadium^{IV} is only adsorbed to a moderate extent. On the other hand, manganese^{II}, cobalt^{II}, nickel and copper^{II} are strongly adsorbed at concentrations of hydrochloric acid less than 0·5 M in presence of 1 M hydrofluoric acid. In fact, a curve for solutions 1 M in hydrofluoric acid and up to 8 M in hydrochloric acid was obtained only for cobalt^{II}, but manganese^{II} [34] and nickel[37] have little tendency to form complexes with fluoride, and the curves obtained for these elements with hydrochloric acid media containing no hydrofluoric acid will not be appreciably changed by the presence of the latter acid. It is evident from Table II that the values of D for manganese^{II} and nickel are scarcely affected by the presence of fluoride ions. Copper^{II} forms the weakly cationic complex CuF^+ with fluoride,[35] but this has obviously little effect on the adsorption of copper^{II} on Zeo-Karb 225 from 1 M hydrofluoric acid (see Table II).

Two values of D are shown in Table II for vanadium^{V}. Distribution coefficients at higher concentrations of acid were not determined, as it was doubtful if they would be reliable. In 3 M hydrochloric acid, about 40 per cent. of the vanadium^{V} is reduced to vanadium^{IV} after being shaken overnight with Zeo-Karb 225.

The curve for iron^{III} in Fig. 4 has an unusual shape, but the increase in the value of D at concentrations of hydrochloric acid greater than 5 M also occurred in absence of hydrofluoric acid (see Fig. 5); similar results for iron^{III} in hydrochloric acid were found by Kraus, Michelson and Nelson[38] with the cation-exchange resin Dowex 50.

As expected, the values of D for aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, nickel and copper^{II} in up to 5 M hydrochloric acid decreased rapidly as the concentration of acid increased; these results are in reasonable agreement with those found by Strelow[18] and by Mann and Swanson,[19] who used Dowex 50 resin.

PROPOSED SEPARATION SCHEME

It is evident from the above results that the best medium in which to separate the constituents of a complex alloy is a solution 1 M in hydrofluoric acid and less than 0·1 M in hydrochloric acid. If such a solution, containing vanadium in the quadrivalent state, were passed through a column of De-Acidite FF in the chloride form and the column were washed with a small volume of 1 M hydrofluoric acid - 0·1 M hydrochloric acid mixture, then titanium^{IV}, zirconium, niobium^{V}, tantalum, molybdenum^{VI} and tungsten^{VI} would be strongly adsorbed on the resin, whereas aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and copper^{II} would pass through.

If the effluent were then passed through a column of Zeo-Karb 225 in the hydrogen form and the column were washed with two volumes of 1 M hydrofluoric acid, vanadium^{IV}, manganese^{II}, cobalt^{II}, nickel and copper^{II} would be retained by the resin, and aluminium, chromium^{III} and iron^{III} would appear in the effluent. Vanadium^{IV} could then be rapidly removed by washing the Zeo-Karb resin with 1 M hydrofluoric - 0·5 M hydrochloric acid mixture.

Treatment of the De-Acidite FF resin with 1 M hydrofluoric acid - 6 M hydrochloric acid mixture would rapidly remove titanium^{IV} and zirconium from the column. Separation

of the four remaining elements into niobium^{V} *plus* tungsten^{VI}, and molybdenum^{VI}, leaving tantalum on the column, should be possible by eluting with 6 M hydrochloric acid - 1 M hydrofluoric acid mixture and then with 2 M hydrochloric acid - 1 M hydrofluoric acid mixture, but it seems likely that these elements would be more readily separated by eluting with solutions of hydrofluoric acid mixed with either ammonium chloride or ammonium fluoride *plus* ammonium chloride. Work on the determination of distribution coefficients for these four elements in such media and on the separation of prepared mixtures and alloy solutions by means of the proposed scheme is in progress.

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The Anion-exchange Separation of Titanium, Zirconium, Niobium, Tantalum, Molybdenum and Tungsten, with Particular Reference to the Analysis of Alloys

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A detailed study has been made of the adsorption of titanium, zirconium, niobium, tantalum, molybdenum and tungsten on the anion-exchange resin, De-Acidite FF, from solutions containing mixtures of two or more of hydrofluoric acid, hydrochloric acid, ammonium fluoride and ammonium chloride, with a view to obtaining a separation scheme for these elements that could be completed within 5 hours. A completely satisfactory separation scheme was achieved, after determining the weight-distribution coefficients of these elements between aqueous solutions of the above reagents and the resin, and after investigating numerous elution curves for these elements from columns of the resin.

Titanium^{IV}, zirconium, niobium^{V}, tantalum, molybdenum^{VI} and tungsten^{VI} were retained on the resin and separated from aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and copper^{II}, by passing a solution of these elements in M hydrofluoric acid, followed by a wash solution of M hydrofluoric acid, through a column of the resin, of 100- to 200-mesh size, in the chloride form. Titanium *plus* zirconium, tungsten, niobium, molybdenum and tantalum were then quantitatively eluted from the resin with 0·01 M hydrofluoric acid - 9 M hydrochloric acid, 3 M hydrofluoric acid - 10 M hydrochloric acid, 0·2 M hydrofluoric acid - 7M hydrochloric acid, 3 M hydrofluoric acid - 3 M hydrochloric acid and M ammonium fluoride - 4 M ammonium chloride mixtures, respectively.

Good results were obtained when the scheme was applied to the separation of these elements in synthetic mixtures and alloys, in which instances spectrophotometric or volumetric methods were used for quantitatively determining the separated elements.

As a result of the determination of the distribution coefficient of metallic ions between an anion-exchange resin and hydrofluoric acid - hydrochloric acid solutions, it was concluded in a previous paper[1] that titanium^{IV}, zirconium, niobium^{V}, tantalum, molybdenum^{VI} and tungsten^{VI} would be readily separated from aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and copper^{II}, by passing these elements, dissolved in M hydrofluoric acid containing less than 0·1 M hydrochloric acid, through a column of De-Acidite FF resin in the chloride form. The first six elements would be adsorbed at the top of the resin column, while the remaining elements would be quickly eluted with M hydrofluoric acid.

The problem now was to elute these six elements successively from the column of anion-exchange resin, before quantitatively determining them. The previous study[1] had indicated that it should be possible to elute titanium^{IV} and zirconium rapidly with a M hydrofluoric acid - 6 M hydrochloric acid mixture, and then to separate the four remaining elements into niobium^{V} *plus* tungsten^{VI}, molybdenum^{VI} and tantalum (left on the column) by eluting with more M hydrofluoric acid - 6 M hydrochloric acid mixture, and then with M hydrofluoric acid - 2 M hydrochloric acid mixture. However, it was felt that a more satisfactory separation scheme would be possible after more distribution coefficients had been determined by using solutions containing ammonium fluoride and chloride besides hydrofluoric and hydrochloric acid.

This further work, complemented by elution studies on columns, which finally led to a completely satisfactory separation within five hours, is described in this Paper.

* This paper reports part of the work carried out by E. J. Dixon for his Ph.D. degree (1963).

EXPERIMENTAL

APPARATUS—

The polythene-ware, shaker, spectrophotometer and pH meter were the same as used in the previous study.[1]

POLYTHENE COLUMNS FOR ANION-EXCHANGE SEPARATIONS—

Columns were designed to permit continuous flow by gravity feed. All joints were of a tight push-fit. Fig. 1 shows the cross-sectional view of a column of dimensions 13 cm × 0·19 sq. cm. The body of the column was a piece of polythene tubing 14 cm long having in internal diameter of 0·50 cm and an external diameter of 0·70 cm. Two discs of diameter 0·60 cm were cut out from polythene sheet of thickness 0·30 cm, and were drilled with about seven holes of diameter about 0·05 cm. One disc was then forced into the bottom of the column until it was about 1·0 cm up the tube, the plane of the disc being at right-angles to the axis of the tube. A few polythene drillings were then packed fairly tightly in this gap and the second disc inserted about 0·3 cm up the tube. This arrangement was sufficient to support the column of resin. A short piece (about 3 cm) of flexible poly(vinyl chloride) tubing of internal diameter about 0·5 cm was pushed over the bottom of the column and fitted with a screw clamp.

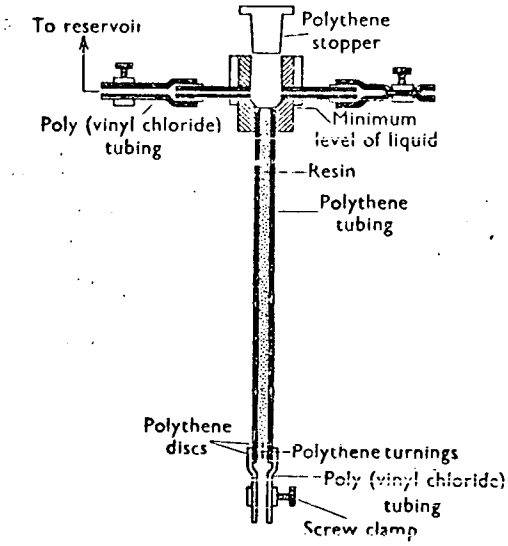

Fig. 1. Cross-section of ion-exchange column

For the fitting at the top of the column, a piece of polythene rod of diameter 1·90 cm and length 3·0 cm with a 0·635-cm diameter hole drilled along its axis was used. The upper end of the column was then forced 1·0 cm into this hole, the remainder of which was then enlarged to a diameter of 0·95 cm and to such a depth that the upper edge of the column tube was neatly chamfered. The upper end of the rod was forced into a 2·0 cm length of polythene tube of 1·90 cm bore and 0·32 cm wall. The top surface was then machined smooth. The purpose of this was to strengthen the fitting.

Six holes of diameter 0·32 cm were then drilled at angles of 60° to each other through the top of the column about 0·5 cm above the top of the column tube. The side arms were made from narrow bore (0·05 cm) polythene tubing, external diameter 0·40 cm, and were forced into each of the six holes until flush with the inside of the column top.

A length of about 2 cm was allowed to project outside the column, and to this was fitted a length of flexible poly(vinyl chloride) tubing, the other end of which was fitted to an outlet tube of polythene welded into the bottom of a 500-ml polythene bottle.

A screw-clamp was fitted near to the lower end of the poly(vinyl chloride) tubing. The head of solution normally applied to the column was about 20 cm. The ribs of a polythene

stopper that is usually fitted to a 100-ml calibrated flask were machined off; the stopper was then coated with a small amount of silicone grease and gently, but firmly, inserted into the top of the column. This formed an airtight seal at the top of the column.

ANION-EXCHANGE RESINS—

De-Acidite FF(Cl), types SRA 70 and SRA 71, were used. The former were used for all determinations of weight-distribution coefficients and early column work. The resins were both 7 to 9 per cent. cross-linked with divinylbenzene, and were identical in all respects except that SRA 70 was 52- to 100-mesh size and SRA 71 was 100- to 200-mesh size. The resin was prepared for use by introducing it into a large glass column as a slurry with water, and back-washing it to remove the finest particles. It was then washed with about four column-volumes of 5 M hydrochloric acid and then with water until the effluent was free from chloride.

For determining distribution coefficients, the resin was dried over anhydrone at 60° C, under reduced pressure.

REAGENTS—

Standard solutions of metals—Standard solutions of iron^{III}, nickel, cobalt^{II}, titanium^{IV} zirconium, niobium^{V}, tantalum, molybdenum^{VI}, and tungsten^{VI}, were prepared as in the previous study.[1]

Other reagents—Hydrofluoric, hydrochloric, nitric and sulphuric acids, and ammonium fluoride and chloride were of analytical-reagent grade.

Reagents and solutions for colorimetric determinations—These were of the purest grade available.

DETERMINATION OF WEIGHT-DISTRIBUTION COEFFICIENTS—

The weight-distribution coefficients were determined by using the same procedure as that adopted in the previous paper.[1]

TREATMENT OF SOLUTIONS BEFORE COLORIMETRIC DETERMINATION—

As hydrofluoric acid readily attacks glass, it was necessary to remove this acid from solutions before performing an analysis, except in the determination of tantalum. If it was known that the colorimetric method was not subject to interference from ions present in Pyrex glass, 1 to 2 ml of concentrated sulphuric acid were added to about 1 g (accurately weighed) of the solution to be analysed in a tall 100-ml Pyrex beaker, and the mixture evaporated until fumes of sulphur trioxide were evolved. (When solutions containing titanium or zirconium are being treated in this manner, it is advisable to pass a flame over the upper half of the beaker, to remove the last traces of hydrofluoric acid.) The solution was cooled, 2 or 3 drops of concentrated nitric acid added to it and the solution strongly boiled until fumes had been evolved for about a minute, to remove as much as possible of the excess of nitric acid. This procedure destroyed the charred products caused by the reaction between fuming sulphuric acid and traces of products from the resin that resulted when strong acids were used in the aqueous phase.

When solutions containing trace amounts of iron, titanium and niobum were analysed, the evaporations were performed in tall 50-ml silica beakers. The sulphuric acid solution was cooled and usually diluted with water, heated until any salts had dissolved and transferred to a graduated flask or analysed in bulk. Solutions of niobium were diluted with 1 per cent. tartaric acid solution, and solutions of tungsten were diluted with concentrated hydrochloric acid. In both instances, warming for a few minutes was necessary to ensure complete dissolution of the element.

This treatment of the solutions before colorimetric determinations was the same for the aqueous phase, which had to be analysed for determinations of weight-distribution coefficients, and for column eluates.

COLORIMETRIC DETERMINATION OF METALS—

Iron^{III}, cobalt^{II}, nickel, molybdenum^{VI}, and tungsten^{VI} were determined in the fluoride-free solutions by the methods outlined in the previous paper.[1] Titanium^{IV}, zirconium and niobium^{V} in fluoride-free solutions and tantalum in fluoride solution were determined by the methods given below.

DETERMINATION OF TITANIUM—

Titanium was determined by using chromotropic acid in an adaptation of the method of Brandt and Preiser.[2] Considerable care was necessary to remove all traces of fluoride from the titanium solution before analysis, because fluoride seriously interferes with the formation of the coloured complex. While fumes of sulphur trioxide are being evolved from the beaker, it is advisable to pass a flame over the upper half of the inside of the beaker to remove the last traces of hydrofluoric acid.

Transfer up to 25 μg of titanium in not more than 4 ml of solution to a 10-ml graduated flask. Add 1 ml of 0·10 per cent. w/v aqueous chromotropic acid and then 3 M sodium acetate until the pH is about 4·5 (*i.e.*, until the red-brown colour first produced is just converted to yellow-brown). Add 2·0 ml of pH 4·5 buffer solution (prepared by dissolving 13·6 g of sodium acetate trihydrate and 8·8 ml of glacial acetic acid in water, and diluting the solution to 250 ml) and dilute to the mark. Measure the optical density at 470 mμ against a reagent blank solution.

Up to 88 μg of zirconium has no effect on this method for the colorimetric determination of titanium, provided that the volume of aqueous chromotropic acid added is increased to 3 ml.

DETERMINATION OF ZIRCONIUM—

Transfer a portion of the solution, containing not more than 60 μg of zirconium, to a 25-ml calibrated flask and add 5 N sulphuric acid or N sodium hydroxide to make the free acid present equivalent to 1 ml of 5 N sulphuric acid. Add 2 ml of 0·10 per cent. w/v xylenol orange,[3] dissolved in 0·01 N sodium hydroxide, from a pipette down the side of the flask (to prevent frothing) and dilute to 25 ml with water. Measure the optical density at 540 mμ against a reagent blank solution.

Up to 10 μg of titanium has no effect on the blank value, or on the optical density due to 44 μg of zirconium.

DETERMINATION OF NIOBIUM—

Niobium was determined by using the method of Freund and Levitt.[4]

By means of pipettes add 5 ml of concentrated hydrochloric acid, 1 ml of freshly prepared 22·5 per cent. stannous chloride solution in concentrated hydrochloric acid, 2 ml of water and 5 ml of acetone to a 25-ml calibrated flask, mixing well after each addition. Add up to 5 ml of niobium solution, 1 per cent. w/v in tartaric acid and 4 per cent. v/v in sulphuric acid, and containing not more than 100 μg of niobium. Add 1 per cent. w/v aqueous tartaric acid solution, containing 4 per cent. v/v sulphuric acid, to give a total volume of 5·0 ml of this solution. Add 5 ml of a freshly prepared 29 per cent. aqueous potassium thiocyanate solution. Dilute to the mark with water and measure the optical density at 385 mμ against a reagent blank solution.

DETERMINATION OF TANTALUM—

In the previous study,[1] tantalum was determined spectrophotometrically at 365 mμ as a complex with pyrogallol,[5] but the sensitivity of the reagent was rather low, and a search was made for a better one. An adaptation of the method of Lauer and Polucktov,[6] in which methyl violet was used, was finally used for determining the distribution coefficients and elution curves.

To a 30-ml polythene bottle, add x ($\leqslant$3·0) g of tantalum solution M in ammonium fluoride, 0·5 x ml of 2 N hydrochloric acid, (3 — 0·5 x) ml of water, (3 — x) ml of M hydrofluoric acid, 2·0 ml of 0·2 per cent. aqueous crystal violet solution and 2·0 ml of pH 2·0 glycine buffer (prepared by dissolving 18·8 g of glycine and 10·7 ml of 11·7 M hydrochloric acid in water and diluting the solution to 250 ml). Add 5 ml of analytical-reagent grade benzene, and shake for two minutes. Set aside for 25 minutes, decant as much as possible of the benzene layer into a 10-ml polythene centrifuge tube, and spin it for about 1 minute. Decant the benzene layer into a 1-cm cell and measure the optical density at 605 mμ against water. Subtract the value of the reagent blank solution.

The optical-density value of 5 μg of tantalum in a 1-cm cell was 0·56.

Although this method was reasonably satisfactory for determining distribution coefficients and elution curves, where errors of up to 20 per cent. can be tolerated, it had its disadvantages for strictly quantitative determinations, since the optical density of the organic phase decreased almost linearly with increasing ammonium chloride concentration in the aqueous

phase, which could contain varying amounts of ammonium chloride. It was found that tantalum could be eluted satisfactorily from a column of anion-exchange resin by using only M ammonium fluoride - 4 M ammonium chloride mixture. Quantitative determinations of tantalum were therefore required in solutions of composition approximately M ammonium fluoride - 4 M ammonium chloride. The method given below was therefore used for quantitative determinations.

Add M ammonium fluoride, 2 M hydrochloric acid, 4 M ammonium chloride and water to a portion of the tantalum solution, so that the total volume is 8 ml and the concentrations of the constituents are equivalent to 3 ml of 4 M ammonium chloride, 3 ml of M ammonium fluoride, 0·25 ml of 2 M hydrochloric acid and 1·75 ml of water. Then add 2 ml of 0·2 per cent. aqueous crystal violet solution, extract the tantalum complex with 5 ml of benzene, and measure the optical density at 605 mμ after 30 minutes.

The optical-density value of 5 μg of tantalum in a 1-cm cell was about 0·38.

The results obtained by using this method were reasonable, giving a precision of about ±0·02 optical density units, which is about ±5 per cent. for 5 μg of tantalum. However, the method has its limitations, since the colour of the solution was still fading slowly even after 30 minutes.

Further work is required on this method before it becomes generally acceptable.

Theory

It is possible to predict quite accurately the volume of eluant needed for obtaining the maximum concentration of an eluted element in the effluent, from a knowledge of its weight-distribution coefficient in that eluant. This is given by the equation below, for low column loadings[1]—

$$v_{max.} = \rho D + i \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where $v_{max.}$ is the volume, in bed-volumes, eluted when the maximum concentration of element is observed in the effluent,

ρ is the density of the resin bed in g per ml,

D is the weight-distribution coefficient of the element between the resin and the solution and

i, in bed-volumes, is the volume of solution in the column, *i.e.*, the volume of solution in, and between, the resin beads and particles, and above and below the resin bed.

The value of D is found by batch-equilibration experiments and is defined by the expression—

$$D = \frac{\text{amount of element on resin per gram of resin}}{\text{amount of element in solution per millilitre of solution}}$$

If w is the weight, in g, of dried resin in the column, v_1 is the volume, in ml, eluted when the maximum concentration of element is observed in the effluent, i_1 is the volume, in ml, of solution in the column and v_b is the volume, in ml, of the resin bed, then—

$$v_{max.} = \frac{v_1}{v_b}, \rho = \frac{w}{v_b} \text{ and } i = \frac{i_1}{v_b}$$

Therefore equation (1) may be rewritten as—

$$v_1 = wD + i_1$$

In all work with columns, the weight of dried resin used for the resin bed was 1 g, and i_1 was approximately 2 ml. Hence v_1 was related to D by the simple equation—

$$v_1 = D + 2$$

D ml of solution must therefore be passed through the column to take an element, whose weight-distribution coefficient in the solution is D, from the top to the bottom of the column. If v ml of this solution is passed down the column ($v < D$), then $\frac{v}{D}$ is the fraction of the column, down which the maximum concentration of the element has travelled. If this fraction is calculated for a metal for each step of an elution sequence, the position of the maximum concentration of element on the column, *i.e.*, the peak of the distribution of element in the band, may be found by adding the fractions. The sum of the fractions may

be represented as $\Sigma\frac{v}{D}$. For an element, which is to be retained by the column, $\Sigma\frac{v}{D}$ must be considerably less than unity.

Results

Distribution coefficients for molybdenum, tungsten, niobium and tantalum between De-Acidite FF and hydrochloric acid - ammonium chloride solutions—

Kraus, Nelson and Moore[7] used M hydrofluoric acid - 4 M ammonium chloride mixture for eluting niobium, and M ammonium fluoride - 4 M ammonium chloride mixture for eluting tantalum. However, they gave no indication of the behaviour of molybdenum and tungsten with such solutions. To see if solutions of these types would be of any value in separating these four elements, distribution coefficients were obtained for these metals in such solutions.

Fig. 2 shows the graphs of the distribution coefficients for these elements between De-Acidite FF and M hydrofluoric acid - 0 to 4 M ammonium chloride mixtures. A comparison of the results of the previous study[1] and Fig. 2 shows that the fluoride complexes of the four elements are displaced from the resin by increasing the chloride-ion concentration, but the formation of the chloro-complexes, which are held by the resin, is suppressed when the hydrogen-ion concentration is small. The tungsten and niobium curves are again similar, and although these ammonium chloride solutions are useful for removing these elements rapidly from the column, they are of no value for separating molybdenum, niobium and tungsten from each other.

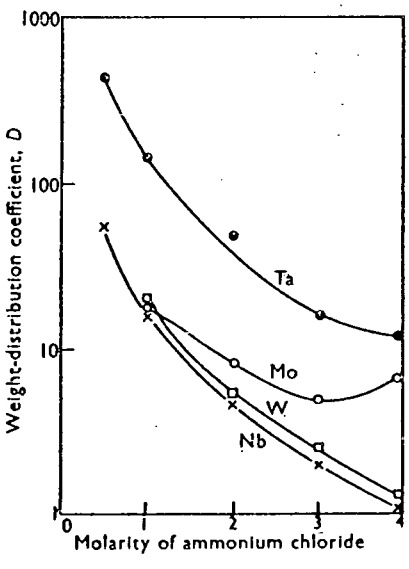

Fig. 2. Weight-distribution curves for tantalum, molybdenum, tungsten and niobium between De-Acidite FF resin and solutions. M in hydrofluoric acid, containing different concentrations of ammonium chloride

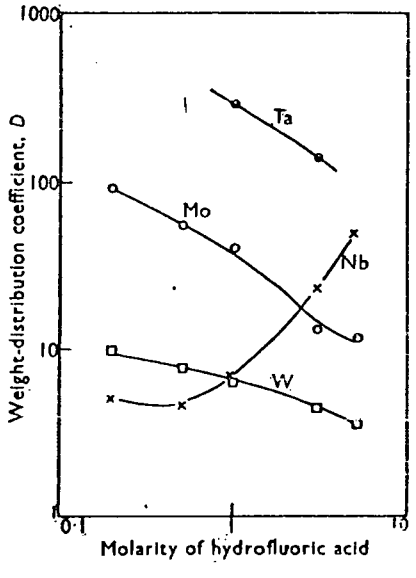

Fig. 3. Weight-distribution curves for tantalum, molybdenum, niobium and tungsten between De-Acidite FF resin and solutions, 6 M in hydrochloric acid, containing different concentrations of hydrofluoric acid

Even in M hydrofluoric acid - 4 M ammonium chloride mixture, tantalum is too strongly held by the resin for rapid elution. Distribution coefficients for tantalum were therefore determined in M hydrofluoric acid - 4 M ammonium chloride mixture, where the acidity was reduced still further by partly neutralising the hydrofluoric acid with ammonia solution. When the concentration of ammonium fluoride was 0·7 M, D for tantalum was 10, and this was reduced to 4 when the concentration of ammonium fluoride was increased to 0·9 M. These results confirm that M ammonium fluoride - 4 M ammonium chloride mixture, for which D is approximately 2, is the best eluting agent for tantalum. Weight-distribution coefficients for molybdenum, niobium and tungsten in this medium were all found to be less than 1.

DISTRIBUTION COEFFICIENTS FOR MOLYBDENUM, TUNGSTEN, NIOBIUM AND TANTALUM BETWEEN DE-ACIDITE FF AND SOLUTIONS OF 6 M HYDROCHLORIC ACID CONTAINING 0·2 TO 5·0 M HYDROFLUORIC ACID—

Kraus and Moore[8] have shown that, in 9 M hydrochloric acid, the adsorption of niobium on Dowex 1 resin varies widely over the range 0·01 to 7 M hydrofluoric acid. The adsorption was at a minimum at about 0·18 M. Tantalum was strongly adsorbed over the whole range, while zirconium was not adsorbed at all. However, they have published no corresponding values for molybdenum and tungsten. As De-Acidite FF is slowly attacked by high concentrations of hydrochloric acid, it was felt desirable to keep the acidity for determinations on the resin as low as possible. Fig. 3, therefore, shows graphs of weight-distribution coefficients for molybdenum, tungsten, niobium and tantalum between De-Acidite FF and solutions in 6 M hydrochloric acid (rather than in 9 M acid), containing 0·2 to 5 M hydrofluoric acid. At higher concentrations of hydrofluoric acid, the values of D for tungsten and niobium diverge widely. However, at the same time, the values of molybdenum become closer to those of tungsten. Neither titanium nor zirconium are adsorbed at all.

A study of the results in the previous paper[1] and Figs. 2 and 3 indicates a basic scheme for the separation of an alloy solution in M hydrofluoric acid. Initially iron, etc., are eluted with M hydrofluoric acid, then titanium *plus* zirconium with, say, 2 M hydrofluoric acid - 6 M hydrochloric acid mixture. Tungsten is eluted with a similar solution, and then niobium with 0·5 M hydrofluoric acid - 6 M hydrochloric acid mixture, and finally molybdenum and tantalum are eluted.

ELUTION STUDIES ON COLUMNS—

Preparation of a column for a separation—The column was filled with resin in the usual way. It was washed with 10 ml of M hydrofluoric acid and then with 10 ml of M ammonium fluoride - 4 M ammonium chloride mixture, to remove any anions that may have been adsorbed on to the resin. The column was then washed with 10 ml of 6 M hydrochloric acid, to ensure that the resin was entirely in the chloride form, and finally with 10 ml of M hydrofluoric acid to remove the hydrochloric acid. The solution was allowed to pass through the column until the level of the liquid was just above the resin.

All column work was done in an efficient fume cupboard.

Addition of metal solutions to the column—The solution of metal ions was transferred to the top of the column (see Fig. 1) in small portions and allowed to run down to the level of the resin. The top of the column was washed three times with about 1-ml portions of M hydrofluoric acid. When the last portion of wash solution was just below the level of the inlet tubes, the polythene stopper, lightly smeared with silicone grease, was slowly inserted into the top of the column. Care was taken to adjust the rate of this insertion to prevent air from being forced into any of the inlet tubes. As soon as the stopper was firmly in position, the clamp on the tube leading from the bottle containing M hydrofluoric acid was opened. The flow-rate could be adjusted, when necessary, by means of the clamp at the bottom of the column.

Determination of elution curves—About 0·5 to 1·0 g of the metal solution in dilute hydrofluoric acid was added to the column, which was then treated, where applicable, with previously determined quantities of earlier eluants and then with the solution for which the elution curve of the metal was to be determined. This effluent was collected in fractions of about 2 g and each was analysed for the metal. The concentration was determined in μg of metal per g of solution, and plotted against the weight of effluent collected, the mid-point of the particular fraction being taken for this purpose.

Elution curve for iron^{III} *with* M *hydrofluoric acid*—As iron is the major constituent of many alloys, it was felt that a large amount of iron should be used for the elution curve as some tailing could be expected with large amounts. An elution curve was obtained for 0·6 g of a solution containing 22 mg of iron, when M hydrofluoric acid was used as eluant. The column dimensions were 13 cm × 0·19 sq. cm, and it contained 1·0 g of De-Acidite FF (SRA 70). The elution curve is shown in Fig. 4 A.

The graph shows that 12 g of M hydrofluoric acid was necessary for the quantitative removal of iron from the column. If the weight of metal solution added to the column exceeds 1·0 g, then a corresponding increase in the weight of M hydrofluoric acid should be taken to ensure the quantitative recovery of iron. The first step in all subsequent elutions was to pass 12 g of M hydrofluoric acid through the column to remove iron, etc.

Elution curves for titanium and tungsten—Hague, Brown and Bright[9] have separated titanium from tungsten by using 2·5 M hydrofluoric acid - 6 M hydrochloric acid mixture, an anion-exchange resin of 200- to 400-mesh size and a flow-rate of approximately 0·08 ml per 0·19 sq. cm per minute. A similar separation was tried with our column, but it was considered unlikely that a complete separation would be achieved if the coarser resin and a faster flow-rate were used. The titanium was eluted with 12·8 g of M hydrofluoric acid, and then with 2 M hydrofluoric acid - 6 M hydrochloric acid mixture: tungsten is slightly more strongly adsorbed in this solution than in 2·5 M hydrofluoric acid - 6 M hydrochloric acid mixture. The elution curve is shown in Fig. 4 A, and the recovery of the titanium was quantitative in 10 g of this eluate. No titanium was found in the first 2·4 g of the 2 M hydrofluoric acid - 6 M hydrochloric acid effluent. Ten grams of 2 M hydrofluoric acid - 6 M hydrochloric acid were therefore considered necessary and sufficient for the quantitative recovery of titanium.

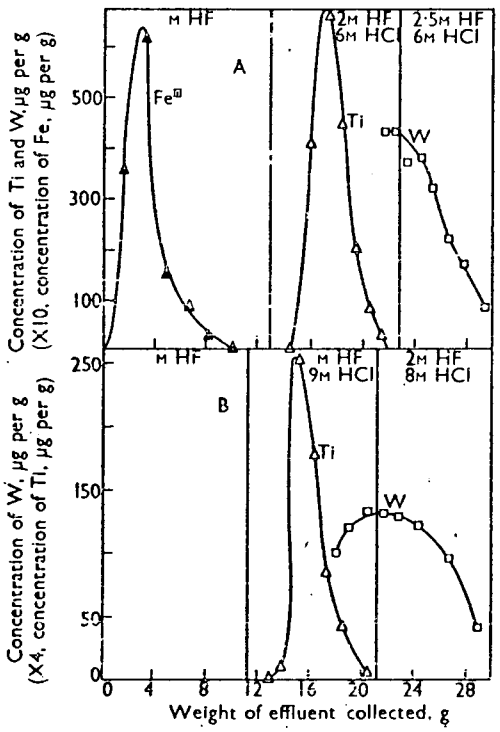

Fig. 4. A, elution curves for iron, titanium and tungsten; eluants as shown. (Average flow-rate, 0·45 g per minute): B, elution curves for titanium and tungsten; eluants as shown. (Average flow-rate, 0·40 g per minute)

The tungsten was eluted with 12 g of M hydrofluoric acid, 10 g of 2 M hydrofluoric acid - 6 M hydrochloric acid mixture, and then with 2·5 M hydrofluoric acid - 6 M hydrochloric acid mixture. Two fractions at the end of the 2 M hydrofluoric acid - 6 M hydrochloric acid effluent were analysed for tungsten, besides the fractions in the 2·5 M hydrofluoric acid - 6 M hydrochloric acid effluent. Part of the elution curve is shown in Fig. 4 A. As was expected, the overlap of the titanium and tungsten was considerable. In fact, 54 per cent. of the tungsten was eluted with the titanium eluant.

It was clear that the 2 M hydrofluoric acid - 6 M hydrochloric acid mixture was not a satisfactory eluant for titanium, since it also slowly removed tungsten from the column. A solution had to be found, in which tungsten was more strongly held by the resin, and from the previous study[1] and Fig. 3, M hydrofluoric acid - 9 M hydrochloric acid mixture

appeared to be the best, since tungsten, niobium, molybdenum and tantalum were all held quite strongly by the resin in the presence of this aqueous phase. Fig. 4B shows the elution curves for titanium and tungsten with M hydrofluoric acid - 9 M hydrochloric acid and 2 M hydrofluoric acid - 8 M hydrochloric acid mixture, respectively. The 2 M hydrofluoric acid - 8 M hydrochloric acid mixture was preferred to the 2·5 M hydrofluoric acid - 6 M hydrochloric acid mixture, since niobium and molybdenum would be more strongly adsorbed from the former solution. The two elution curves were obtained from separate experiments. Again considerable overlap of the curves occurred, only 55 per cent. of the tungsten being recovered in the 2 M hydrofluoric acid - 8 M hydrochloric acid effluent. The titanium recovery was quantitative in 10 g, as before.

Table I shows that the elution maxima for tungsten obtained in Figs. 4 A and B agree well with the values calculated by using the equation—

$$v_1 = D + 2.$$

TABLE I

COMPARISON OF PRACTICAL AND THEORETICAL ELUTION MAXIMA FOR TUNGSTEN

Eluant	$D + 2$	Elution maximum, ml
2 M hydrofluoric acid - 6 M hydrochloric acid mixture ..	7	7 to 8
M hydrofluoric acid - 9 M hydrochloric acid mixture ..	10	10

As 10 to 12 g of eluant were required to remove completely an element whose value of D was about unity, it was necessary that any element that was to remain on the column, should have a value of D greater than 20 and, probably, considerably more than 20. The results in the previous study[1] and those given in Fig. 3 indicated no conditions under which the value of D for tungsten is greater than 20, while, at the same time, those for titanium and zirconium are about unity. More work on distribution coefficients was therefore necessary.

DISTRIBUTION COEFFICIENTS FOR MOLYBDENUM, TUNGSTEN, NIOBIUM AND TANTALUM BETWEEN SOLUTIONS OF 9 M HYDROCHLORIC ACID CONTAINING 0·01 TO 3·0 M HYDROFLUORIC ACID AND DE-ACIDITE FF—

The weight-distribution coefficients for molybdenum, tungsten, niobium and tantalum are plotted *versus* the logarithm of the variable hydrofluoric acid concentration in Fig. 5. Neither titanium nor zirconium were adsorbed by the resin from any of the solutions indicated. Both molybdenum and tantalum are strongly adsorbed over the whole range. In 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture, molybdenum, tungsten, niobium and tantalum are all strongly adsorbed by the resin, and so this was the mixture chosen for eluting titanium and zirconium.

FURTHER ELUTION CURVES—

Fig. 6 A shows the elution curves for zirconium, tungsten and niobium when these ions were eluted successively with M hydrofluoric acid, 0·01 M hydrofluoric acid - 9 M hydrochloric acid, 2 M hydrofluoric acid - 8 M hydrochloric acid and 0·5 M hydrofluoric acid - 6 M hydrochloric acid mixtures. The recovery of zirconium was complete in 10 g of effluent, and tungsten was quantitatively recovered in 18 g of 2 M hydrofluoric acid - 8 M hydrochloric acid mixture. However, the recovery of niobium with 0·5 M hydrofluoric acid - 6 M hydrochloric acid mixture was only 81 per cent., the remainder having been eluted with the 2 M hydrofluoric acid - 8 M hydrochloric acid mixture. 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture was a satisfactory eluant for titanium and zirconium, and 12 g were collected in subsequent elutions.

Selection of suitable eluants for tungsten and niobium—A study of Fig. 5 shows that two possibilities exist for separating niobium and tungsten from each other, *viz.*, either (*a*) eluting tungsten with 2 or 3 M hydrofluoric acid - 9 M hydrochloric acid mixture, and then eluting niobium with 0·2 M hydrofluoric acid - 9 M hydrochloric acid or 0·5 M hydrofluoric acid 6 M hydrochloric acid mixtures, or (*b*) eluting niobium with 0·1 or 0·2 M hydrofluoric acid - 9 M hydrochloric acid mixture and then eluting tungsten with 2 or 3 M hydrofluoric acid - 9 M hydrochloric acid mixture.

Table II summarises the differences in the values of D for niobium and tungsten in these media.

TABLE II

COMPARISON OF DISTRIBUTION COEFFICIENTS FOR NIOBIUM AND TUNGSTEN IN VARIOUS MEDIA

Solution mixture	D for tungsten	D for niobium
0·1 M hydrofluoric acid - 9 M hydrochloric acid ..	45	7
0·2 M hydrofluoric acid - 9 M hydrochloric acid ..	28	3·5
2·0 M hydrofluoric acid - 9 M hydrochloric acid ..	5	28
3·0 M hydrofluoric acid - 9 M hydrochloric acid ..	4	50

At first sight, it would seem best to elute tungsten first with 3 M hydrofluoric acid - 9 M hydrochloric acid mixture, since the difference between the D values of niobium and tungsten is greatest in this medium. However, it is clear that when the eluant is changed from 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture to 3 M hydrofluoric acid - 9 M hydrochloric acid mixture, the concentration of a small portion of solution, where these two eluants mix, will have the approximate composition of a 0·2 M hydrofluoric acid - 9 M hydrochloric

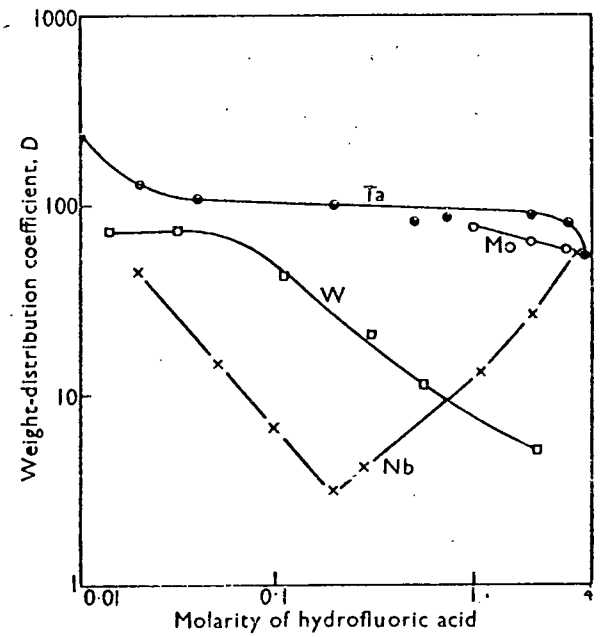

Fig. 5. Weight-distribution curves for tantalum, molybdenum, tungsten and niobium between De-Acidite FF resin and solutions, 9 M in hydrochloric acid, containing different concentrations of hydrofluoric acid

acid mixture, from which niobium is only slightly adsorbed. Further, when the eluant is changed from M hydrofluoric acid to 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture, a similar situation arises. Although it would be preferable to avoid passing through such adsorption minima, that caused by the second change of eluant is inevitable. The adsorption minimum caused by the first change of eluant can be avoided if niobium is eluted before tungsten, but in this instance the separation factor is worse. Both tungsten and molybdenum pass through a minimum when the eluant is changed from M hydrofluoric acid to 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture, but the effect is less pronounced for tungsten and considerably less pronounced for molybdenum.

To increase the separation factor for niobium, it was decided to reduce the flow-rate during the addition of the sample solution to the column and during the passage of one

column - volume (about 2 ml) after changing the eluant, when this change of eluant meant that a point of minimum adsorption for niobium, or any other element, was about to occur.

(*i*) *Elution of tungsten before niobium*—Fig. 6 B shows the elution curve for niobium when it was eluted successively with M hydrofluoric acid, 0·01 M hydrofluoric acid - 9 M hydrochloric acid, 3 M hydrofluoric acid - 9 M hydrochloric acid and 0·5 M hydrofluoric acid - 6 M hydrochloric acid mixtures. The flow-rate during the addition of the sample to the column and immediately after the first two changes of eluants was reduced to about 3 drops per minute (0·2 g per minute) from the normal flow-rate of 6 drops per minute.

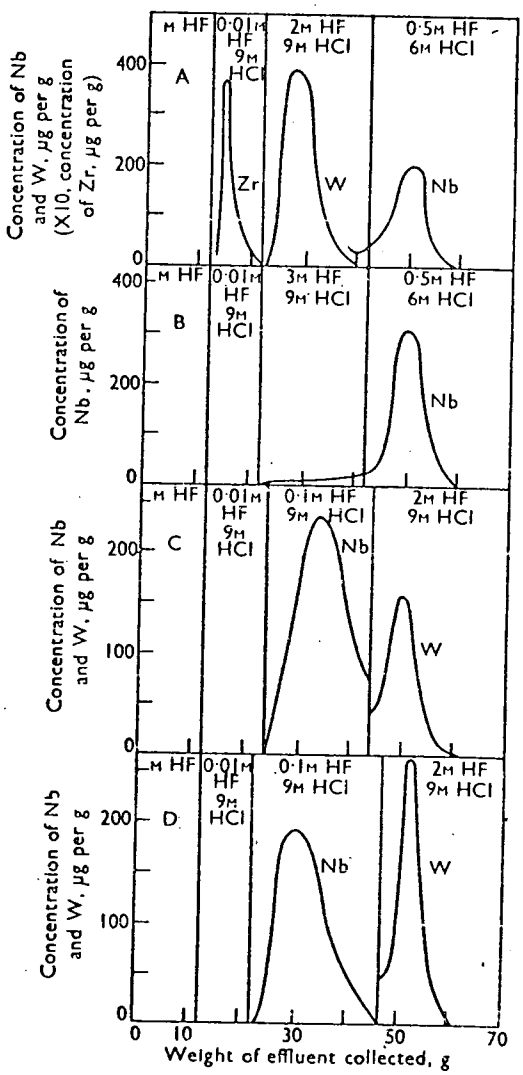

Fig. 6. A, elution curves for zirconium, tungsten and niobium; eluants as shown. (Average flow-rate, 0·40 g per minute): B, elution curves for niobium; eluants as shown. (Average flow-rate, 0·45 g per minute): C, elution curves for niobium and tungsten; eluants as shown. (Average flow-rate, 0·45 g per minute): D, elution curves for niobium and tungsten; eluants as shown. (Average flow-rate, 0·35 g per minute.)
Column dimensions: A, B and C, 13 cm × 0·19 sq. cm; D, 21 cm × 0·11 sq. cm

The 0·5 M hydrofluoric acid - 6 M hydrochloric acid effluent contained 92 per cent. of the niobium, the remainder being found in the 3 M hydrofluoric acid - 9 M hydrochloric acid effluent. It would seem that some of the niobium had been carried near to the bottom of the column as its adsorption passed through these two minima, and was being progressively washed off with the 3 M hydrofluoric acid - 9 M hydrochloric acid eluant.

(*ii*) *Elution of niobium before tungsten*—Fig. 6 C shows the elution curves for niobium with 0·1 M hydrofluoric acid - 9 M hydrochloric acid mixture, and for tungsten with 2 M hydrofluoric acid - 9 M hydrochloric acid mixture, when a solution containing both niobium and tungsten was separated on a column of De-Acidite FF under conditions similar to those used to obtain the results given in Fig. 6 B. The niobium band was rather broader than expected, and 6 per cent. of the niobium had still not been eluted after 20 g of 0·1 M hydrofluoric acid - 9 M hydrochloric acid mixture had been passed through the column. Thirty per cent. of the tungsten was eluted before the change to 2 M hydrofluoric acid - 9 M hydrochloric acid eluant.

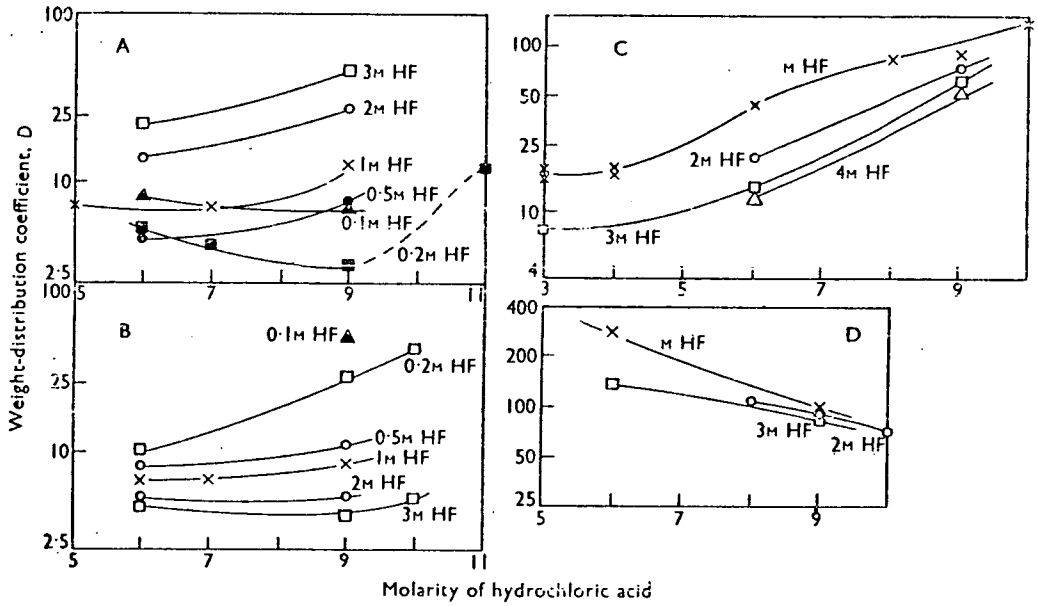

Fig. 7. Weight-distribution coefficients for: A, niobium; B, tungsten; C, molybdenum; and D, tantalum between De-Acidite FF resin and solutions containing fixed concentrations of hydrofluoric acid and different concentrations of hydrochloric acid

(*iii*) *Elution of niobium before tungsten on a longer column*—The columns used for all the above work were operated at a flow-rate of up to 6 drops per minute. Since the flow-rate could be increased to about 10 drops per minute when the tap at the foot of the column was fully open, it was obvious that a longer column giving a maximum flow-rate of 6 drops per minute could readily be constructed. Such a column, which should lead to an improved separation,[10] was constructed from polythene tube of internal diameter 3·5 mm and had dimensions of 21 cm × 0·11 sq. cm. In all other respects this column was identical to the columns used previously. The column also contained 1 g of dried resin and gave a flow-rate of 6 drops per minute under the usual head of about 20 cm of solution.

Fig. 6 D shows the elution curves for niobium and tungsten under conditions used to obtain Fig. 6 C, except that the longer column was used and 25 g of effluent were collected for the niobium fraction. The niobium recovery was almost quantitative (about 99 per cent.) and 80 per cent. recovery of tungsten was a considerable improvement on the results shown in Fig. 6 C.

At this stage, it was fairly certain that, if the separation of tungsten before niobium was carried out on the longer column, the recovery of niobium in the 0·5 M hydrofluoric acid - 6 M hydrochloric acid effluent (see Fig. 6 B) would be more quantitative. However, it was

decided to examine in detail all the information that had been obtained on distribution coefficients to see if better eluants for quantitatively separating niobium before tungsten could be found, since by using this sequence of elutions, the adsorption of niobium passes through only one minimum, but when tungsten is eluted, the niobium passes through two adsorption minima.

Discussion of distribution coefficients

Although Figs. 3 and 5 show how the hydrofluoric acid concentration affects the distribution coefficients of molybdenum, tungsten, niobium and tantalum, it is not easy to see from these graphs how the hydrochloric acid concentration affects the values of D. The values of D obtained from the previous study[1] and Figs. 3 and 5 are re-plotted together with some extra results, in Figs. 7 A, B, C and D, *versus* the hydrochloric acid concentration, each line having a constant hydrofluoric acid concentration. It was seldom easy to make up metal solutions more concentrated than 10 M in hydrochloric acid, and when the molarity of hydrofluoric acid exceeded 2, it was not easy to make the hydrochloric acid concentration exceed 9 M.

The retention of tungsten in the separation shown in Fig. 6 D would be improved by using 0·2 M hydrofluoric acid - 10 or 11 M hydrochloric acid mixture for eluting niobium. The values of D for niobium in Fig. 7 A tend to increase at the higher hydrochloric acid concentrations. Further, tantalum is less strongly held as the hydrochloric acid concentration increases, although molybdenum is more strongly adsorbed.

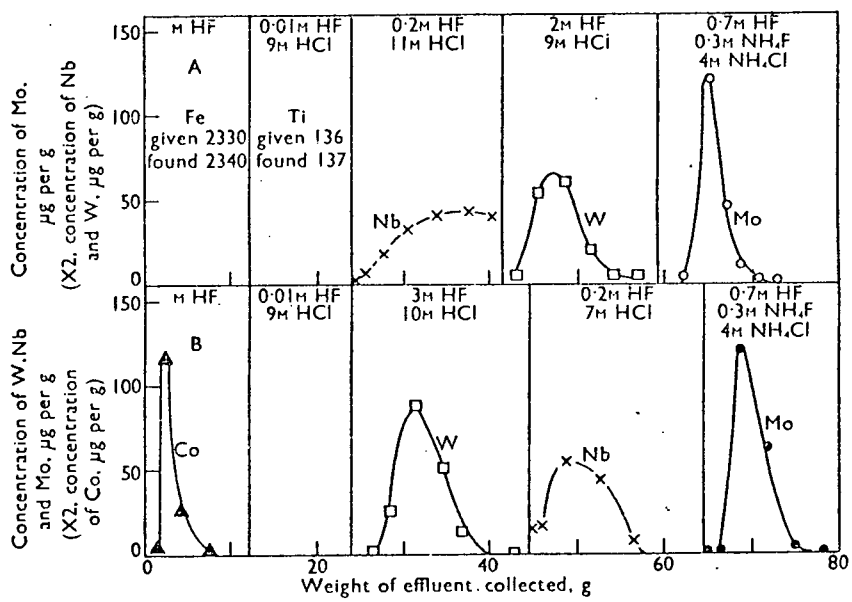

Fig. 8. A, recoveries for iron and titanium, and elution curves for niobium, tungsten and molybdenum; eluants as shown. (Average flow-rates, 0·48 g per minute for molybdenum and 0·25 g per minute for the rest): B, elution curves for cobalt, tungsten, niobium and molybdenum; eluants as shown. (Average flow-rates, 0·30 g per minute for cobalt and tungsten, 0·36 g per minute for niobium and 0·56 g per minute for molybdenum)

Fig. 8 A shows the recoveries of iron and titanium, and the elution curves for niobium, tungsten and molybdenum, when a solution containing these five elements was separated with M hydrofluoric acid, and 0·01 M hydrofluoric acid - 9 M hydrochloric acid, 18 g of 0·2 M hydrofluoric acid - 11 M hydrochloric acid, 18 g of 2 M hydrofluoric acid - 9 M hydrochloric acid and 0·7 M hydrofluoric acid - 0·3 M ammonium fluoride - 4 M ammonium chloride mixtures, respectively. The recoveries of iron, titanium, tungsten and molybdenum were all quantitative, but only 74 per cent. of the niobium was recovered in the 0·2 M hydrofluoric

acid - 11 M hydrochloric acid fraction. The recovery of molybdenum was completely satisfactory, since no trace of molybdenum could be detected in the first 1·0 g of effluent after the eluant had been changed to the 0·7 M hydrofluoric acid - 0·3 M ammonium fluoride - 4 M ammonium chloride mixture. The elution curve for niobium indicates that at least 27 and possibly 30 g of 0·2 M hydrofluoric acid - 11 M hydrochloric acid mixture are necessary for complete elution of the niobium. This would almost certainly involve considerable early elution of tungsten and excessive movement of tantalum on the column, and so 0·2 M hydrofluoric acid - 11 M hydrochloric acid mixture was considered unsuitable as an eluant for niobium.

Table III gives a comparison of the three eluants used so far for niobium, together with two possible alternatives.

TABLE III

COMPARISON OF VARIOUS ELUTING SOLUTIONS FOR NIOBIUM

Figure	6C	6D	8A	—	—
Molarity of hydrofluoric acid	0·1	0·1	0·2	0·2	0·2
Molarity of hydrochloric acid	9	9	11	11	10
Volume of effluent, v	17	21·5	15	22·5	17
D for niobium	7	7	11	11	5
D for tungsten, D_W	45	45	55	55	40
$\Sigma(v/D_W)$	0·38	0·48	0·27	0·41	0·43
Niobium eluant v/D_W	0·65	0·75	0·54	0·68	0·70
Niobium found, per cent.	94	99	74	—	—
Tungsten found, per cent.	70	80	100	—	—
Height of column, cm	13	21	21	21	21

The values of $\Sigma(v/D_W)$ for 27 g (22·5 ml) of 0·2 M hydrofluoric acid - 11 M hydrochloric acid mixture, and 20 g (17 ml) of 0·2 M hydrofluoric acid - 10 M hydrochloric acid mixture that would be necessary for quantitatively eluting niobium are only slightly lower than the value for 25 g (21·5 ml) of 0·1 M hydrofluoric acid - 9 M hydrochloric acid mixture, in which the recovery of tungsten was 80 per cent. It was considered that the slightly improved retention of the tungsten was not sufficient for a quantitative separation.

Attention was now returned to the alternative of eluting tungsten before niobium.

A study of the distribution coefficients of tungsten, niobium, molybdenum and tantalum for various possible eluants for tungsten, the results of which are given in Table IV, shows that the best solution for eluting tungsten before niobium is 3 M hydrofluoric acid - 10 M hydrochloric acid mixture. (Some of the values in this Table are approximate extrapolations from Figs. 7 A, B, C and D.)

TABLE IV

COMPARISON OF THE DISTRIBUTION COEFFICIENTS FOR TUNGSTEN, NIOBIUM, MOLYBDENUM AND TANTALUM

Eluant for tungsten	Distribution coefficients for—			
	tungsten	niobium	molybdenum	tantalum
2 M hydrofluoric acid - 9 M hydrochloric acid	5	28	70	90
3 M hydrofluoric acid - 9 M hydrochloric acid	4	50	57	83
4 M hydrofluoric acid - 9 M hydrochloric acid	4	80	51	60
3 M hydrofluoric acid - 10 M hydrochloric acid	5	60	90	70
4 M hydrofluoric acid - 10 M hydrochloric acid	5	80	80	50

A similar study of Table V shows that 0·2 M hydrofluoric acid - 7 M hydrochloric acid mixture is the most suitable eluant for niobium.

A solution containing cobalt, tungsten, niobium and molybdenum was separated on a 21-cm column of De-Acidite FF by using the solutions listed below for eluting the different fractions: 12 g of M hydrofluoric acid for cobalt, 12 g of 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture for titanium and zirconium, 20 g of 3 M hydrofluoric acid - 10 M hydrochloric acid mixture for tungsten, 20 g of 0·2 M hydrofluoric acid - 7 M hydrochloric acid mixture for niobium and 16 g of 0·7 M hydrofluoric acid - 0·3 M ammonium fluoride - 4 M ammonium chloride mixture for molybdenum. The elution curves for cobalt, tungsten, niobium and molybdenum are shown in Fig. 8 B. The recoveries of cobalt, tungsten and

molybdenum were quantitative, and the early elution of niobium was reduced to about 6 per cent. Since the 3 M hydrofluoric acid - 10 M hydrochloric acid mixture is the optimum eluant for tungsten and the loss of niobium was small, it was thought that if 100- to 200-mesh resin was used in place of 52- to 100-mesh resin, the separation would be made quantitative.

TABLE V

COMPARISON OF THE DISTRIBUTION COEFFICIENTS FOR NIOBIUM, MOLYBDENUM AND TANTALUM

Eluant for niobium	Distribution coefficients for—		
	niobium	molybdenum	tantalum
0·2 M hydrofluoric acid - 6 M hydrochloric acid ..	5	30	400
0·5 M hydrofluoric acid - 6 M hydrochloric acid ..	5	55	300
0·2 M hydrofluoric acid - 7 M hydrochloric acid ..	4	95	250
0·5 M hydrofluoric acid - 7 M hydrochloric acid ..	5	70	200
0·2 M hydrofluoric acid - 9 M hydrochloric acid ..	3	100	100

None of the ammonium chloride solutions used for obtaining the results shown in Fig. 2 gave a sufficient difference in D values between tantalum and molybdenum to permit their separation to be made by using reasonable flow-rates. However, a study of the results of the previous paper[1] and Figs. 7 C and D indicates that 3 M hydrofluoric acid - 3 M hydrochloric acid mixture is the best eluant for molybdenum; D for molybdenum is about 6, whereas that for tantalum is about 200.

SEPARATIONS IN WHICH 100- TO 200-MESH RESIN WAS USED IN THE SHORT COLUMNS—

An average flow-rate in our resin columns of less than 6 drops per minute was undesirable, since it would mean that a separation and subsequent determination of six elements would not be achieved in a working day. Under a 20-cm head of solution, a flow-rate of 6 drops per minute was not possible with the 21-cm column filled with 100- to 200-mesh resin. However, if the 13-cm column packed with 100- to 200-mesh resin was used, an average flow-rate of 6 drops per minute was achieved under a 20-cm head, with the screw clamp on the tube at the bottom of the column fully open.

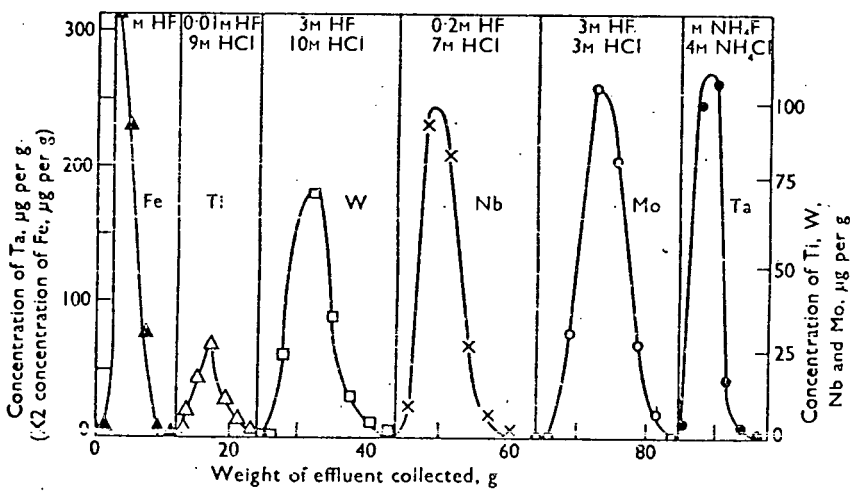

Fig. 6. Elution curves for the separation of a mixture containing iron, titanium, tungsten, niobium, molybdenum and tantalum; eluants as shown

A solution containing iron^{III}, titanium, tungsten, niobium, molybdenum and tantalum in dilute hydrofluoric acid was separated on the short column containing 100- to 200-mesh De-Acidite FF into six separate effluents, by successively using 12 g of M hydrofluoric acid, and 12 g of 0·01 M hydrofluoric acid - 9 M hydrochloric acid, 20 g of 3 M hydrofluoric acid - 10 M hydrochloric acid, 20 g of 0·2 M hydrofluoric acid - 7 M hydrochloric acid, 20 g of 3 M hydrofluoric acid - 3 M hydrochloric acid and 17 g of ammonium fluoride - 4 M ammonium

chloride mixtures. Each effluent was collected in 6 to 8 fractions, and the elution curves obtained for each of the six metals are shown in Fig. 9. The recoveries of all six elements were quantitative, and no early elution of any element could be detected. The molybdenum curve was rather broader than those for tungsten and niobium, but 20 g of 3 M hydrofluoric acid - 3 M hydrochloric acid mixture was sufficient for the full recovery of molybdenum. Thirteen grams of M ammonium fluoride - 4 M ammonium chloride mixture was sufficient to remove all the tantalum.

The recoveries of the six metals, together with the average flow-rates and times taken for the various elutions, are shown in Table VI.

TABLE VI

RECOVERIES OF IRON, TITANIUM, TUNGSTEN, NIOBIUM, MOLYBDENUM AND TANTALUM AFTER ANION-EXCHANGE SEPARATION

	Iron	Titanium	Tungsten	Niobium	Molybdenum	Tantalum
Average flow-rate, g per minute ..	0·21	0·29	0·33	0·38	0·50	0·65
Time for fraction, minutes ..	55	41	60	53	40	26
Metal added, μg	2161	124	442	630	819	1132
Metal found, μg	2225	126	462	632	788	1100

The satisfactory recoveries of molybdenum and tantalum, and the symmetrical shape of their elution curves justified the use of the higher flow-rates.

The total time taken for the separation was 4½ hours and this was considered to be satisfactory.

CONCLUSIONS ON ELUTION STUDIES

It can now be concluded from all of the elution studies described above that, for the column conditions used by us, the *D* values for elements to be retained on the resin column, must be as high as possible and certainly greater than 50. The *D* value for an element that is to be removed from the resin colmun should be as low as possible, and be preferably less than 5.

As the *D* value for an element to be removed increases, the elution curve becomes broader. For examples of this, see Fig. 6 D, where *D* for niobium is 7, Fig. 8 A where *D* for molybdenum is 2 and *D* for tungsten is 5, but *D* for niobium is 12, and Fig. 9 where the *D* values of iron and titanium are less than or equal to 1, but *D* for molybdenum is 6.

METHOD FOR SEPARATING TITANIUM, ZIRCONIUM, NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN FROM THE REMAINING CONSTITUENTS OF AN ALLOY AND FROM EACH OTHER—

Construct a polythene column of dimensions 13 cm × 0·19 sq. cm, as described on page 186, fill it with 1·00 ± 0·05 g of dry, 100- to 200-mesh De-Acidite FF (SRA 71) and wash the resin column as described on page 187. Add dropwise to the column a portion (by weight) of 0·5 to 1·0 g of a solution containing about 15 mg of alloy per g of approximately M hydrofluoric acid. Open the outlet tap so that the flow-rate is about, but does not exceed, 3 drops per minute and collect the effluent in a dry, weighed 30-ml polythene bottle. Allow the level of the solution to fall just to the top of the resin bed. Carefully fill the top of the column with M hydrofluoric acid from a side-tube, and allow the level of the solution to fall to the top of the resin bed again. Wash traces of solution on to the resin column twice more with M hydrofluoric acid. When the level of the liquid has fallen just below the side-tubes, insert the stopper (lightly coated with silicone grease) slowly but firmly, and then immediately open the tap from the M hydrofluoric acid stock-bottle.

Now open the tap at the bottom of the column fully so that the flow-rate is about 6 drops per minute. Collect a total of 12 g (12 ml) of this effluent containing the iron, chromium, nickel, cobalt, copper, manganese, aluminium and vanadium[IV]. Then close the tap from the M hydrofluoric acid stock-bottle, and immediately open the tap from the 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture stock-bottle. Partially close the tap at the bottom of the column so that the flow-rate is reduced to between 2 and 3 drops per minute, and change the receiver to another 30-ml polythene bottle. After 10 minutes open the tap at the bottom of the column fully, so that the flow-rate is again about 6 drops per minute. When a total of 12 g (11 ml) of this effluent, containing titanium, zirconium and vanadium[V],

has been collected, change the eluant to 3 M hydrofluoric acid - 10 M hydrochloric acid mixture, again reduce the flow-rate to between 2 and 3 drops per minute and change the receiver to another 30-ml polythene bottle. After 10 minutes increase the flow-rate to about 6 drops per minute. When 20 g (18 ml) of this effluent, containing tungsten, has been collected, change the eluant to 0·2 M hydrofluoric acid - 7 M hydrochloric acid mixture and change the receiver to another 30-ml polythene bottle. Collect 20 g (18 ml) of the eluate, containing niobium, at the rate of 6 drops per minute. Change the eluant to 3 M hydrofluoric acid - 3 M hydrochloric acid mixture and collect 20 g (20 ml) of the eluate, containing molybdenum, in a polythene bottle at the rate of 6 drops per minute. Change the eluant to M ammonium fluoride - 4 M ammonium chloride mixture, and immediately change the receiving vessel. Collect 13 g (12 ml) of effluent, containing tantalum, in a polythene bottle.

TABLE VII

RESULTS OBTAINED FROM THE ANALYSIS OF SYNTHETIC SOLUTIONS

All figures are expressed in μg

	Iron	Nickel	Titanium	Tungsten	Niobium	Molybdenum	Tantalum
Taken	14,210	—	—	445	—	783	—
Found	14,420	—	—	445	—	771	—
Error	(+1·5%)	—	—	0	—	−12	—
Taken	20,023	—	601	403	562	710	299
Found	20,460	—	600	396	547	698	312
Error	(+2%)	—	−1	−7	−15	−12	+13
Taken	—	1711	—	643	515	—	—
Found	—	1726	—	632	528	—	—
Error	—	+15	—	−11	+13	—	—
Taken	189	986	16·0	370	311	—	8·0
Found	—	—	14·2	381	330	—	10·0
Error	—	—	−1·8	+11	+19	—	+2·0
Taken	3710	—	—	4·5	292	7·9	156
Found	—	—	—	4·4	314	9·0	153
Error	—	—	—	−0·1	+22	+1·1	−3

The collecting vessels were all calibrated at the appropriate volumes so that the amount of effluent collected was within ± 1 ml of the optimum volume.

NOTES—

1. If the flow-rate is not reduced at the start of the collections of the titanium and tungsten eluates, losses of niobium may occur.
2. The capacity of the resin is 3·5 milliequivalents per dry gram; 1 g of resin, for a 1 per cent. loading (single charge), will therefore accommodate the weights of strongly adsorbed metals (if adsorbed singly) listed below: titanium, 1·7 mg; zirconium, 3·2 mg; tungsten, 6·4 mg; niobium, 3·3 mg; molybdenum, 3·4 mg; and tantalum, 6·3 mg.
3. The total column loading of strongly adsorbed metals must not exceed 5 per cent., and preferably should not exceed 3 per cent.
4. As the resin is slowly attacked by the strong acids, it is advisable to change the resin after about 2 months' use.
5. It is possible to leave a trace of metal solution at the top of the column during a separation; this would be washed on to the resin during the next separation. Although the loss will be less than 0·1 per cent. of the solution added, and so could not be detected even in a volumetric analysis, it can become important when a trace of a metal is analysed in the next separation. Therefore it is advisable, when the composition of the alloy is greatly different from that of the previous alloy, to wash the top of the column several times with M hydrofluorice acid, allowing the washings to pass through the resin bed, which is then treated with 10 ml of M hydrofluoric acid and 12 ml of M ammonium fluoride - 4 M ammonium chloride mixture. This operation will remove traces of any metal left at the top of the column from the previous separation. The stopper should also be cleaned thoroughly between separations.
6. If a metal is known to be absent, the particular step in the elution sequence may be omitted.
7. If a determination of titanium and zirconium is not required, the 0·01 M hydrofluoric acid - 9 M hydrochloric acid elution may be omitted, and the titanium and zirconium eluted together with tungsten, with whose spectrophotometric determination they will not interfere.
8. If the determination of tungsten and niobium is not required, or if one is absent, the element (or elements) can be eluted with 25 g of 0·5 M hydrofluoric acid - 7 M hydrochloric acid mixture, without affecting the molybdenum or tantalum. However, no solution could be found that would elute niobium and molybdenum together without affecting the retention of the tantalum.
9. If a determination of the metals towards the end of the sequence is not required, they may be eluted together with M ammonium fluoride - 4 M ammonium chloride mixture.

Analysis of synthetic solutions

The metals in a number of synthetic solutions, containing widely different amounts of titanium, tungsten, niobium, molybdenum and tantalum, were separated by using the proposed scheme, and the separated elements were determined spectrophotometrically by the methods described earlier. For the spectrophotometric determinations of iron, titanium and niobium, part or all of the effluents were evaporated to a small volume in silica beakers and heated with 1 ml of concentrated sulphuric acid until fumes of sulphur trioxide appeared. The nickel, molybdenum and tungsten effluents were treated in a similar way, but Pyrex glass beakers instead of silica beakers were used. Fractions of the tantalum effluents were analysed directly. Table VII shows the recoveries for five synthetic solutions.

These recoveries were considered to be reasonable. In most instances, the errors were within the limits of error attributable to the spectrophotometric determinations. The first two synthetic mixtures gave good recoveries for all the elements strongly adsorbed on the resin column from M hydrofluoric acid, when the amount of iron added to the column was large. Twenty milligrams of iron would give a column loading of about 10 per cent. for a singly charged complex if the iron were strongly adsorbed, but since the distribution coefficient of iron^{III} in M hydrofluoric acid is less than 1, the column loading is probably under 5 per cent.

Analysis of alloys

Method for dissolving an alloy—

Weigh accurately 0·5 to 1·0 g of the alloy into a 100-ml polytetrafluoroethylene beaker, add about 10 ml of 40 per cent. w/w hydrofluoric acid (in a fume cupboard) and carefully add 2 to 3 ml of nitric acid, sp.gr. 1·42, a few drops at a time, covering the beaker with a nylon cover. Most alloys dissolve in about 2 minutes. Heat the beaker and contents on a hot-plate to break down any carbides, and evaporate almost to dryness to remove as much as possible of the excess of nitric acid. Warm the residue with about 15 ml of M hydrofluoric acid and transfer the solution to a dry, weighed 30-ml polythene bottle. Most, if not all, of the salts should have redissolved. If necessary, dissolve the remainder by warming with a further 5 ml of M hydrofluoric acid, and transfer the solution to the polythene bottle. Wash the beaker twice with M hydrofluoric acid, and add the washings to the polyethylene bottle to make a total volume of about 30 ml. Re-weigh the bottle, and hence calculate the concentration of the alloy in mg of alloy per g of solution.

Note—

If the iron concentration of the alloy is more than 60 per cent., only 0·5 g of alloy should be dissolved in 30 ml of solution, since iron^{III} fluoride is not too soluble in M hydrofluoric acid. Steels and ferro-alloys normally gave a clear solution with up to 1·0 g of alloy per 30 ml of solution.

Table VIII

Results obtained for the analysis of mild steels

Alloy	Metal	Certificate composition, per cent.	Found, per cent.			
British Chemical Standard No. 273 ..	Tungsten	0·28	0·277,	0·272,	0·283	
	Niobium	0·000$_8$	<0·001,	<0·001,	<0·001	
	Molybdenum	0·04$_5$	0·041,	0·041,	0·043	
British Chemical Standard No. 275 ..	Tungsten	0·05	0·043,	0·041,	0·042	
	Niobium	0·03$_5$	0·035,	0·043,	0·043,	0·039
	Molybdenum	0·09$_5$	0·094,	0·091,	0·088,	0·094
British Chemical Standard No. 276 ..	Tungsten	0·20	0·196,	0·191,	0·189	
	Niobium	0·05$_5$	0·054,	0·048,	0·050	
	Molybdenum	<0·01	0·004,	0·003,	0·004	
British Chemical Standard No. 277 ..	Titanium	0·03$_5$	0·035,	0·038,	0·039	
	Tungsten	0·12	0·126,	0·110,	0·121	
	Niobium	0·02$_1$	0·020,	0·025,	0·027	
	Molybdenum	0·01$_5$	0·011,	0·012,	0·013	

Analysis of steels—

Four mild steels, containing about 98 per cent. of iron and traces of other metals, were analysed by the proposed method. Spectrophotometric finishes were used for determining

the separated elements. Because the elements that are strongly adsorbed on De-Acidite FF resin were present in only trace amounts, about 4 g of the alloy solution (instead of 0·5 to 1·0 g) were added to the column in several portions. Under these circumstances, 16 g of M hydrofluoric acid were passed down the column to ensure complete removal of iron and other non-absorbed metals. The results are given in Table VIII.

These results, obtained for the determination of titanium, niobium, molybdenum and tungsten in these mild steels, were considered to be satisfactory. No results are reported for tantalum in these steels, because their tantalum contents were too low (of the order of 0·01 per cent.) to be determined with even moderate precision by using the spectrophotometric method described earlier (p. 188).

There is no doubt that tantalum in the tantalum effluents could be determined with an accuracy and precision of $\pm 0{\cdot}001$ per cent. for the tantalum content of the steel, if a more reliable spectrophotometric method for determining traces of tantalum was available.

VOLUMETRIC FINISH FOR THE DETERMINATION OF THE MAJOR CONSTITUENTS OF AN ALLOY—

Pure solutions of iron^{III}, titanium^{IV}, niobium^{V}, molybdenum^{VI} and tungsten^{VI} in hydrofluoric acid - hydrochloric acid mixtures are suitable for determining the metal by a volumetric reduction method. Headridge and Taylor[11] have shown that niobium^{V} in 0·5 M hydrofluoric acid - 6 M hydrochloric acid solution is quantitatively reduced in a Jones reductor to niobium^{III}. The reduced species is collected in ammonium ferric sulphate solution, and the equivalent amount of ferrous iron thus produced is titrated with standard dichromate solution. Similar methods have been devised by the same workers[12,13] for iron^{III}, tungsten^{VI} and molybdenum^{VI} in fluoride solutions, by using a Jones reductor or a silver reductor.

Such volumetric methods are suitable for determining major constituents (10 to 100 per cent.) of an alloy after anion-exchange separation. Three such alloys were analysed, and the results of the volumetric determinations are shown in Table IX.

TABLE IX

RESULTS OBTAINED FROM THE ANALYSIS OF ALLOYS BY USING A VOLUMETRIC FINISH AFTER ANION-EXCHANGE SEPARATIONS

Alloy	Element	Certificate value, %	Found, %
B.C.S. 241/1 (Cr–V–W–Co–Mo steel)	Tungsten	19·61	19·57, 19·64
B.C.S. 231/2 (Ferro-molybdenum)	Molybdenum	70·1	70·2, 70·2
	Iron	28·9*	28·8, 28·9
Ferro-niobium-tantalum†	Niobium	59·1	59·2, 59·3

* Value obtained by Headridge and Taylor.[13]
† Supplied by London and Scandinavian Metallurgical Co. Ltd.

The volumetric determinations were considered to be completely satisfactory and to furnish conclusive proof of the clean separation of all of the metals by the scheme described in this paper. As the separations are quantitative, the accuracy and precision of an analysis is dependent only on the accuracy and precision of the final determination of a metal in the pure solution.

EFFECT OF OTHER METALS ON THE SEPARATION SCHEME—

Several elements, such as boron, lead, magnesium, phosphorus, silicon, sulphur and tin, that can be encountered in steels, high-temperature and ferro-alloys, have not been studied in this work. Of these only boron and tin might cause interference.

Boron—Boron forms an anionic complex with hydrofluoric acid and would be adsorbed by the anion-exchange resin from M hydrofluoric acid. However, as it is not complexed by chloride, it would be displaced from the resin along with titanium and zirconium by the 0·01 M hydrofluoric acid - 9 M hydrochloric acid mixture.

Tin—Kraus and Nelson[14] have reported distribution coefficients for tin^{IV} in hydrofluoric acid - hydrochloric acid solutions. A study of their results shows that tin^{IV} would be eluted with molybdenum by 3 M hydrofluoric acid - 3 M hydrochloric acid mixture. The recovery of tin would probably be quantitative in the molybdenum fraction.

Conclusions

The method described should be useful for determining titanium, zirconium, niobium, tantalum, molybdenum and tungsten in steels, high-temperature and ferro-alloys, and could be readily adapted for determining these elements in ores, mineral dressings and other materials.

The analysis of a complex alloy can be completed by two chemists in a working day.

While it would certainly be quicker to determine these elements in alloys by using instrumental techniques such as emission spectrography, X-ray fluorescence spectrography and atomic-absorption spectroscopy, the method should be useful for the analysis of standard alloys, and for non-routine analysis of special alloys, where the use of an instrumental technique is not justified.

We thank Mr. M. S. Taylor for performing the volumetric determinations. We gratefully acknowledge the receipt of a research grant from Thos. Firth and John Brown Ltd., Sheffield, to maintain one of us (E. J. D.).

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3

THE ANALYTICAL APPLICATIONS OF REDOX REACTIONS IN HYDROFLUORIC ACID

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The complexing properties of fluoride have not been widely applied in analysis because, in acid solution, fluoride ions combine with hydrogen ions to produce undissociated hydrofluoric acid which attacks glassware. With cheap polyethylene and polypropylene apparatus now available, the use of fluoride as a complexing agent in acid solution is no longer troublesome.

Niobium, tantalum, and tungsten are among the most difficult metals to get into and keep in acidic solution. The soluble chloride and sulphate complexes of these elements in their highest and most stable oxidation states are readily hydrolysed in solutions of all but the most concentrated acids, and the hydrolysed species polymerize to produce precipitates of the hydrated oxides. A similar phenomenon occurs when alkaline solutions containing soluble niobate, tantalate or tungstate are acidified. Niobium and tantalum can, of course, be retained in acidic solution for some time as soluble complexes of oxalic, tartaric and other organic acids, but complete dissolution is only attained if a bisulphate melt of these metals is dissolved in the presence of the organic complexing agent or if an alkaline solution containing niobate or tantalate is acidified in the presence of tartrate, etc. Tungsten can be retained in acid solution as phosphotungstic acids, but these acids are large molecules containing 3, 9 or 12 WO_3 groups for each phosphorus atom and reduction of these species appears to be slow.

Hydrofluoric acid will, however, readily dissolve niobium pentoxide, tantalum pentoxide and tungsten trioxide, provided that they have not been strongly fused, and the metals will stay in solution indefinitely. The complex anions thus produced appear to be mononuclear. The reduction of niobium(V) and tungsten(VI) in hydrofluoric acid solutions has been studied in detail.

The most suitable medium for the reduction of niobium(V) to niobium(III) is 6 *M* hydrochloric–0.5 *M* hydrofluoric acid[1]. Up to 60 mg of niobium pentoxide can be completely reduced on passage through a Jones reductor (38 cm long, 1.8 cm internal diameter, 16–30 mesh zinc shot) amalgamated to the extent of 0.75% (w/w). The effluent is collected in ferric ammonium sulphate solution containing phosphoric acid under oxygen-free nitrogen, and the ferrous iron produced is titrated with standard potassium dichromate solution.

For years, attempts to determine tungsten by titration of the tungsten(III), produced by reduction of tungsten(VI) with metals, were unsuccessful[2], because reduction was not quantitative. Very recently, GEYER AND HENZE[3] and LUKE[4] showed that almost complete reduction can be achieved if strong hydrochloric acid

solutions of tungsten(VI) are reduced. We have found that tungsten(VI) (up to 18 mg of tungsten trioxide) in 2 *M* hydrochloric acid–0.5 *M* hydrofluoric acid can also be reduced completely to tungsten(III) by the above-mentioned Jones reductor. The reduced species was again collected in ferric ammonium sulphate solution containing phosphoric acid. Some results are shown in Table I.

TABLE I

RECOVERY OF TUNGSTEN TRIOXIDE

Tungsten trioxide		*Deviation*
taken mg	*recovered* mg	mg
3.56	3.58	+0.02
4.44	4.45	+0.01
6.70	6.70	0.00
11.05	11.03	−0.02
12.61	12.63	+0.02
14.57	14.56	−0.01
15.53	15.53	0.00
16.91	16.88	−0.03

The volumetric determination of molybdenum(III), after reduction of molybdenum(VI) by passage through a Jones reductor, has been employed since at least 1930, when DÖRING[5] studied the procedure. Complete reduction to the trivalent state is also achieved under exactly the same conditions as those found satisfactory for tungsten(VI).

The reduction is complete for amounts of molybdenum(VI) up to at least 20 mg (Table II).

TABLE II

RECOVERY OF MOLYBDENUM TRIOXIDE

Molybdenum trioxide		*Deviation*
taken mg	*recovered* mg	mg
5.32	5.32	0.0
7.96	7.97	+0.01
8.65	8.65	0.0
10.95	10.93	−0.02
13.45	13.46	+0.01
15.12	15.10	−0.02
17.91	17.91	0.0
20.30	20.29	−0.01

It has been shown above that hydrofluoric acid can be used to keep niobium, tantalum and tungsten in solution and allows satisfactory volumetric methods for niobium and tungsten. Fluoride forms complexes with many other elements, and in certain cases, displaces the redox potentials for half-reactions in such a way that new volumetric procedures become possible.

The stability constants for the monofluoride complexes of several elements are shown in Fig. 1. Most of these were taken from *Stability Constants*[6] but a few have been estimated from the data of BABKO[7].

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It may be noted that the monofluoride complexes of monovalent and divalent ions are, except for beryllium and tin(II), of low stability; the fluoride complexes of trivalent and tetravalent ions are much more stable. Values for the stability constants of higher fluoride complexes are less complete but it is obvious that in

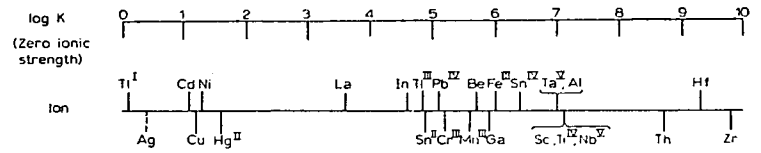

Fig. 1. Stability constants of some monofluoride complexes. The log K values for Cd, Ni, Tl(III), Pb(IV), Mn(III), Be, Sn(IV), Ta(V), Ti(IV), Nb(V) and Hf have been estimated.

many cases the overall stability constant for a particular species, say MF_4^{-x} or MF_6^{-y} will be sufficiently large for fluoride to have a considerable effect on the redox potential for a couple. For example, the reduction potentials of the iron(III)-iron(II) couple (millimolar in both ions) are +0.68 and +0.10 V in 0.5 *M* sulphuric acid and in 0.5 *M* hydrofluoric acid–0.5 *M* ammonium fluoride respectively.

The reduction potentials for a number of other couples in fluoride solution have also been measured in our laboratory and these results are given in Table III. Some standard reduction potentials for uncomplexed ions are given for comparison.

TABLE III

System	*Ratio of concentrations* $M_{ox}:M_{red}$ *mmoles/l*	*Solution composition*	*Temp.* °C	*Reduction potential* V	$E°$ *for uncomplexed ions*
Mn^{+3}/Mn^{+2}	1:1	0.5 *M* NH_4F–0.5 *M* HF	25	+0.87	+1.51
Mn^{+7}/Mn^{+3}	1:1	0.5 *M* NH_4F–0.5 *M* HF	25	+1.30	+1.51
Cr^{+6}/Cr^{+3}	1:1	0.5 *M* NH_4F–0.5 *M* HF	25	+0.95	+1.33
Sn^{+4}/Sn^{+2}	1:1	0.5 *M* NH_4F–0.5 *M* HF	25	+0.05	+0.15
Mo^{+6}/Mo^{+3}	0.2:1	2.0 *M* HCl–0.5 *M* HF	12	+0.04	—
W^{+6}/W^{+3}	0.25:1	2.0 *M* HCl–0.5 *M* HF	12	0.00	—
Nb^{+5}/Nb^{+3}	0.11:1	6.0 *M* HCl–0.5 *M* HF	12	+0.02	—

The reduction potentials of the couple $H^+/\frac{1}{2}H_2$ under the conditions prevalent in 2 *M* hydrochloric acid–0.5 *M* hydrofluoric acid and 6 *M* hydrochloric acid–0.5 *M* hydrofluoric acid are estimated to be +0.22 V and +0.27 V respectively.

These results indicate the possibility of developing several new volumetric methods, but the most interesting couples are the two manganese ones. In 0.5 *M* hydrofluoric acid–0.5 *M* ammonium fluoride, manganese(II) should be oxidised to manganese(III) with permanganate and this is indeed so. The absorption spectra of the manganese(III) fluoride complex and of potassium permanganate are shown in Fig. 2. These indicate that a photometric titration of manganese(II) with permanganate will be satisfactory in the region 450–650 mμ. The molar extinction coefficient of manganese(II) in the visible region of the spectrum is very low. Fig. 3 illustrates the photometric titration of 3.49 mg of manganese(II) with standard potassium permanganate solu-

tion, the EEL Titrator and an Ilford No. 604 filter being used. The reaction appears to be selective for manganese(II) in the presence of other elements and offers a possibility for the direct titration of manganese in ferromanganese and steels. We are at present working on such determinations. Some results for the determination of manganese(II) alone and in the presence of certain other elements are given in Table IV.

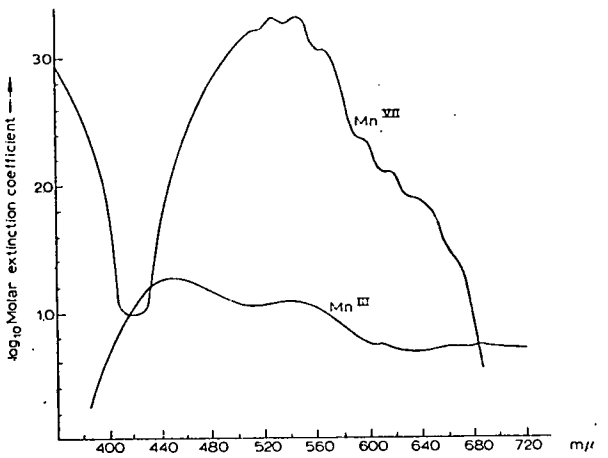

Fig. 2. Absorption spectra of Mn(III) and Mn(VII) in 1 *M* hydrofluoric acid.

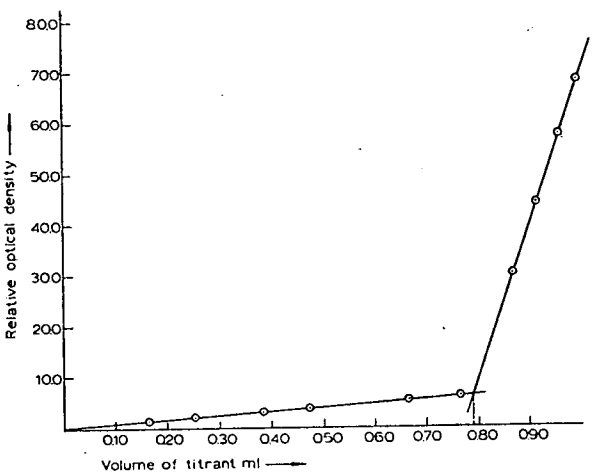

Fig. 3. Photometric titration of manganese(II) (3.49 mg) in presence of chromium(III) (11.38 mg), nickel(II) (5.43 mg) and cobalt(II) (6.36 mg) with 0.02 *M* potassium permanganate solution.

Incidentally, the titration of manganese(II) in fluoride solution with permanganate was described by ZVENIGORODSKAYA[8] in 1946, but this simple method for the determination of manganese does not appear to have been widely noticed.

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Finally, with regard to the titration of niobium(III), tungsten(III) and molybdenum(III), it should be noted that the reduced species are not stable in acid solution even in the absence of oxygen. They are oxidised with varying speeds by hydrogen ion. This point is illustrated in Fig. 4. A consideration of the redox potentials of the appropriate couples, as given in Table III, shows that this is to be expected.

TABLE IV

RECOVERY OF MANGANESE

Nickel taken mg	*Chromium taken mg*	*Cobalt taken mg*	*Manganese*		*Deviation mg*
			taken mg	*recovered mg*	
—	—	—	2.12	2.12	0.00
—	—	—	2.77	2.76	−0.01
—	—	—	4.29	4.33	+0.04
—	—	—	5.12	5.14	+0.02
7.51	—	—	3.65	3.65	0.00
10.70	—	—	3.08	3.06	−0.02
—	5.69	—	3.50	3.50	0.00
—	8.25	—	2.08	2.07	−0.01
—	—	5.63	2.59	2.56	−0.03
—	—	7.23	4.03	4.04	+0.01
6.35	6.83	4.63	2.45	2.45	0.00
5.43	11.38	6.36	3.49	3.50	+0.01

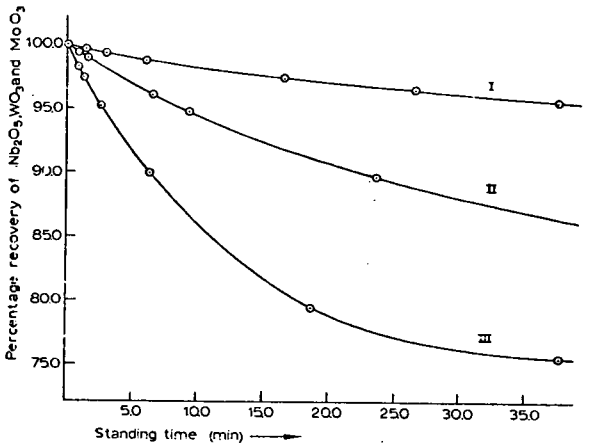

Fig. 4. Recovery-time curves for the Nb(III), W(III) and Mo(III) species. I. Mo(III) in 2.0 *M* HCl–0.5 *M* HF; II. Nb(III) in 6.0 *M* HCl–0.5 *M* HF; III. W(III) species in 2.0 *M* HCl–0.5 *M* HF.

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4

The Volumetric Determination of Niobium in the Presence of Tantalum

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A volumetric method for the determination of niobium is described. Niobium^{V} in 6 M hydrochloric - 0·5 M hydrofluoric acid solution is reduced quantitatively in a Jones reductor to niobium^{III}. The solution containing the niobium^{III} species is collected in ammonium ferric sulphate solution, in which an amount of ferrous iron is produced equivalent to the amount of niobium present. The ferrous iron is determined by titration with 0·1 N potassium dichromate. Amounts of niobium from 1·0 to 50 mg have been determined alone and in the presence of different amounts of tantalum. The method has been applied to the determination of niobium in ferrous and non-ferrous alloys.

Although the volumetric determination of niobium has been studied by many workers since 1885, no completely satisfactory procedure has so far been reported. Methods for this determination are based on the titration of a solution of niobium after treatment with a metallic reducing agent to convert the element into the tervalent state. The early methods, reviewed by Schoeller and Waterhouse,[1] all yielded low results, probably because of the presence of a colloidal phase of niobic acid resulting from hydrolysis. A more satisfactory volumetric method, proposed and used by Cunningham,[2] was studied in detail by Knowles and Lundell.[3] These workers examined the reduction of niobium^{V} in sulphuric acid media and used succinic acid and hydrogen peroxide as complexing agents, but their results, although indicating almost complete reduction, lacked precision.

As the most stable complex of niobium in aqueous media is probably the fluoro complex, we have examined the volumetric determination of niobium in fluoride-containing media.

Materials used

Apparatus—

Because of the corrosive nature of hydrofluoric acid solutions towards glassware, the apparatus used was constructed entirely in polythene.

The reductor column was prepared from heavy-gauge polythene tubing (length 60 cm; internal diameter 1·80 cm) narrowing rapidly at the base to a polythene stopcock, and a delivery tube 12 cm long and of internal diameter 6 mm was used. Polythene tubing (6 mm bore) was wrapped round the column from top to bottom, and cold water was passed through this tubing to maintain a cool, constant temperature within the column during reduction. The collecting vessel was a 250-ml polythene bottle fitted with a polythene screw-cap having three holes in the top to accommodate the delivery tube from the column and inlet and outlet tubes for nitrogen.

Reagents—

Nitrogen—This was oxygen-free "spot" nitrogen obtained from the British Oxygen Co. Ltd.

Hydrofluoric and other acids—These were of analytical-reagent grade.

Potassium dichromate solution—An exactly 0·1000 N solution of potassium dichromate was prepared from the analytical-reagent grade salt

1 ml ≡ 4·646 mg of niobium.

Zinc shot—Two sizes of AnalaR zinc shot obtained from Hopkin & Williams Ltd. were used; these were 8 to 16 mesh (batch No. 33018) and 16 to 30 mesh (batches Nos. 41935 and 51838).

Niobium and tantalum pentoxides—These were Specpure materials, obtained from Johnson, Matthey and Co. Ltd. Standard solutions of niobium and tantalum were prepared by dissolving accurately weighed amounts of the pentoxides in boiling hydrofluoric acid (40 per cent. w/w) in a 100-ml polytetrafluoroethylene beaker. The solutions were diluted to suitable volumes, adjusted to 0·5 M in hydrofluoric acid and stored in screw-cap polythene bottles.

Oxygen-free distilled water—This was prepared by boiling distilled water vigorously for 15 minutes and allowing it to cool under liquid paraffin; the water was stored under liquid paraffin.

PREPARATION OF AMALGAMATED ZINC SHOT—

The zinc shot was amalgamated to the extent of 0·75 per cent. w/w by vigorously shaking 500 g of shot—previously washed with dilute hydrochloric acid (2 + 98) and then with distilled water—with 250 ml of a 2 per cent. w/v solution of mercuric chloride in a stoppered flask for 45 to 60 seconds. The supernatant solution was discarded, and the shot was washed several times with distilled water and then once with dilute sulphuric acid (2 + 98). The shot was then washed with distilled water and stored under dilute hydrochloric acid (1 + 99).

PRELIMINARY EXPERIMENTS

The initial experiments were carried out in sulphuric acid media 0·5 M in hydrofluoric acid, and 8- to 16-mesh zinc shot was used. Approximately 20-mg amounts of niobium pentoxide in 75 ml of the solution being examined were passed through the reductor, and then 75 ml of the same solution were passed through as wash solution. The total volume was collected in a mixture of 25 ml of 0·04 N ammonium ferric sulphate and 30 ml of orthophosphoric acid, sp.gr. 1·75, under an atmosphere of nitrogen. The solution was diluted to 250 ml with oxygen-free distilled water, and the amount of ferrous iron present (equivalent to the amount of niobium^{III} produced) was determined by titration with 0·1 N potassium permanganate. For solutions 0·5 M in hydrofluoric acid, the results, each of which is the mean of three determinations, were—

Concentration of sulphuric acid, M	2	4	6	7	8
Recovery of niobium pentoxide, %	67·0	91·8	95·5	Reaction too vigorous	

Reduction of niobium^{V} in hydrochloric - hydrofluoric acid media was then examined under identical experimental conditions. The ferrous iron produced was titrated with 0·1 N potassium dichromate, with an aqueous 0·2 per cent. w/v solution of barium diphenylaminesulphonate as indicator. For solutions 0·5 M in hydrofluoric acid, the results were—

Concentration of hydrochloric acid, M	2	4	6	8
Recovery of niobium pentoxide, %	—	95·5	96·5	94·7

For these hydrochloric - hydrofluoric acid media, the volumes of 0·1 N potassium dichromate needed for oxidising the constant amount of indicator used in each determination, *i.e.*, the blank titre, were greater than was expected from theory. The calculated value was 0·04 ml, whereas, for 150 ml of 6 M hydrochloric - 0·5 M hydrofluoric acid diluted to 250 ml, 0·18 ml was needed. Further work with 5·00-ml portions of standard ammonium ferrous sulphate solution showed that the titre needed to reach the equivalence point as given by the change in colour of the indicator increased with increasing concentration of chloride in the titrand. However, by using a photometric method of end-point detection under identical conditions in the absence of any indicator, a constant titre was obtained regardless of the concentration of chloride ion. The results are shown in Table I, in which the values for the visual titration are corrected for a theoretical blank value of 0·04 ml; redistilled analytical-reagent grade hydrochloric acid was used.

After the results have been corrected for the calculated indicator blank of 0·04 ml, as in Table I, it is obvious that the presence of chloride ion in the titrand causes the change

TABLE I

TITRES OBTAINED WITH DIFFERENT MEANS OF END-POINT DETECTION

Hydrochloric acid present, M	Sulphuric acid present, M	Titre of 0·1 N potassium dichromate: End-point found visually, ml	Titre of 0·1 N potassium dichromate: End-point found photometrically, ml
0·0	1·0	4·76	4·75
0·5	0·0	4·84	—
1·0	0·0	4·89	4·75
3·0	0·0	4·94	4·74

in colour to occur after the true equivalence point. On the other hand, it was found that an increase in the concentration of sulphuric acid in a chloride-free solution did not affect the end-point in this way. Why chloride ion should so influence the end-point is not obvious, but, because of this effect, it is necessary to re-determine the blank value each time the concentration of hydrochloric acid in the titrand is changed.

Reduction of niobium^{V} in hydrofluoric acid and also in fluoroboric - hydrofluoric acid media was examined, but reduction to the tervalent state was found to be far from complete; the results were—

Concentration of acid, M	2·0	4·0	6·0
Recovery from hydrofluoric acid, %	40·8	—	48·5
Recovery from fluoroboric acid, %	—	56·6*	—

* The solution in this experiment was also 0·5 M in hydrofluoric acid.

It was evident from these results, and from those on p. 44, that the most suitable medium for reduction of niobium^{V} was 6 M hydrochloric - 0·5 M hydrofluoric acid, and a series of determinations with approximately 20-mg amounts of niobium pentoxide in this medium gave a recovery of 96·5 $\pm$ 0·1 per cent. The reason for the consistent but slightly low recovery was not apparent until it was appreciated that perhaps a small amount of the niobium^{III} species was being oxidised by hydrogen ion during passage of the niobium^{III} - acid medium through the delivery tube below the zinc shot. The mean time for this part of the process, calculated from the rate of flow, was 6 minutes. By replacing the delivery tube and stopcock with a short piece of narrow-bore tubing that just protruded into the collecting vessel, it was possible to decrease this time to a few seconds. Under these conditions, recovery of niobium was quantitative, the average recovery in twelve determinations for amounts of niobium pentoxide between 18 and 22 mg being 99·9 per cent. with a maximum error of 0·2 per cent.

In order to determine small amounts of niobium pentoxide it was necessary to decrease the magnitude of the blank value. This was achieved by using a shorter column (38 cm long), with the result that the volume of 6 M hydrochloric - 0·5 M hydrofluoric acid solution used could be decreased from 150 to 80 ml. The blank value was thereby decreased from 0·18 to 0·10 ml.

Reduction in the short column with a fresh batch of 8- to 16-mesh zinc shot (batch No. 51050) was not quantitative, and satisfactory recoveries could not be obtained when this shot was used in the longer column. This, in our opinion, was due to the quality of the shot, a large proportion of which were hollow, which increased the total effective surface area. This resulted in a lighter coating of amalgam, thereby increasing the reactivity of the shot when in contact with acid in the column. With a heavier coating of mercury, this shot would possibly have given quantitative recoveries.

Satisfactory results were obtained when the smaller zinc shot (16 to 30 mesh) was used in the shorter column, and this shot showed more consistency between batches (batches Nos. 49135 and 51838 were used).

The final variable examined was the time needed for quantitative reduction. Previous workers[3] have stated a minimum of 25 minutes, but we found that recovery was quantitative even with a time as short as 6 minutes (see Table II).

TABLE II

EFFECT OF TIME OF REDUCTION ON RECOVERY OF NIOBIUM PENTOXIDE

Time of reduction, minutes	Niobium pentoxide taken, mg	Niobium pentoxide found, mg	Difference, mg
34	19·78	19·80	+0·02
28	19·90	19·82	−0·08
27	21·13	21·13	0·0
26	19·33	19·33	0·0
25	20·05	20·08	+0·03
22	20·96	20·95	−0·01
16	22·20	22·22	+0·02
13	17·00	17·02	+0·02
12	20·00	20·00	0·0
10	21·93	21·95	+0·02
6	18·20	18·21	+0·01

Method

Dissolve the niobium pentoxide residue by boiling with 5 to 10 ml of 40 per cent. hydrofluoric acid, evaporate the solution almost to dryness in a platinum crucible, add 10 ml of dilute hydrofluoric acid (11 + 89), and transfer the solution to a 2-oz polythene bottle marked at 50 ml. Rinse the crucible with 10 ml of water, and add the rinsings to the solution in the polythene bottle; then add 26·5 ml of hydrochloric acid, sp.gr. 1·18, dilute to the 50-ml mark with water, and mix thoroughly.

After water has run through the cooling system for some minutes, wash the reductor column with 150 ml of 6 M hydrochloric - 0·5 M hydrofluoric acid solution, and discard the washings. When all but the last few millilitres of wash solution has entered the column, adjust the flow of nitrogen to a steady 200 to 250 ml per minute, and attach to the base of the column a 250-ml polythene collecting bottle containing 25 ml of 0·04 N ammonium ferric sulphate and 30 ml of orthophosphoric acid, sp.gr. 1·75.

Introduce the niobium^{V} solution into the top of the column in 5- to 10-ml portions, and maintain a constant depth of solution above the zinc shot. Take 30 ml of 6 M hydrochloric - 0·5 M hydrofluoric acid wash solution, and rinse the 2-oz polythene bottle with three 5-ml portions; pour these rinsings on to the column, allowing the level of the solution in the column to fall almost to the zinc shot before adding the next portion. Add the remaining 15 ml of wash solution in a similar manner. When the level of the final 5-ml portion has almost reached the zinc shot, unscrew the collecting vessel; rinse the nitrogen-flow tube with oxygen-free distilled water during removal of the bottle.

Dilute the solution in the collecting bottle to 230 to 240 ml with oxygen-free distilled water, and add exactly 5 drops (0·25 ml) of an aqueous 0·2 per cent. w/v solution of barium diphenylaminesulphonate as indicator. Titrate the solution with 0·1000 N potassium dichromate to a permanent purple end-point; add titrant from a 5- or 10-ml microburette (grade A). Subtract from the titre the blank value determined as described below.

Pass identical volumes (80 ml) of 6 M hydrochloric - 0·5 M hydrofluoric acid solution through the column as described above, and collect as usual. To three individual solutions, add 2·50, 5·00 and 10·00 ml of 0·10 N ammonium ferrous sulphate, and titrate as described above. The difference between the titres for the solutions containing 5·00 and 10·00 ml of the ferrous solution subtracted from the titre for that containing 5·00 ml gives the blank value. Similarly, calculate the blank value from the titres for the solutions containing 2·50 and 5·00 ml of the ferrous solution. Both blank values should be the same.

Notes—

1. It is advisable to carry out the method with two standard amounts of niobium pentoxide to check that the column is working satisfactorily before samples having unknown niobium contents are analysed.

2. Zinc dissolves during reduction, and it is necessary to replenish the column to its original length with fresh amalgamated zinc shot after eight or nine determinations.

3. After forty to fifty determinations, the amount of free space in the column has increased to an extent such that it is advisable completely to empty the shot from the column and to re-pack with the same shot.

Results

The proposed method was applied to the determination of niobium, both alone and in the presence of different amounts of tantalum; the results are shown in Tables III and IV.

In order to apply the method to the analysis of metallurgical products, it was necessary to isolate the mixed oxides of niobium and tantalum from other reducible impurities, which

Table III

Recovery of niobium pentoxide in absence of tantalum

Niobium pentoxide—			Niobium pentoxide—		
taken, mg	recovered, mg	Difference, mg	taken, mg	recovered, mg	Difference, mg
1·55	1·51	−0·04	18·91	18·90	−0·01
3·04	3·01	−0·03	22·93	22·94	+0·01
5·39	5·39	0·0	30·60	30·63	+0·03
9·26	9·25	−0·01	38·00	37·99	−0·01
10·78	10·78	0·0	42·63	42·66	+0·03
13·92	13·94	+0·02	54·37	54·40	+0·03
15·02	15·01	−0·01			

TABLE IV

RECOVERY OF NIOBIUM PENTOXIDE IN PRESENCE OF TANTALUM

Tantalum pentoxide present, mg	Niobium pentoxide— taken, mg	recovered, mg	Difference, mg
49·36	1·97	1·96	−0·01
42·30	13·53	13·56	+0·03
28·77	24·34	24·33	−0·01
16·96	38·23	38·23	0·0
2·50	47·31	47·29	−0·02

would obviously interfere. The hydrolysis method described by Bagshawe and Elwell[4] was used for this purpose, with slight modification in the initial dehydration, the solution being evaporated until fumes of perchloric acid were evolved[5] before hydrolysis with sulphur dioxide solution, in an attempt to prevent co-precipitation of titanium, if present. Recovery of niobium and tantalum by this method was checked by analysing a sample prepared from Specpure oxides; the results are shown in Table V.

TABLE V

RESULTS FOR PREPARED MIXTURE OF OXIDES

Samples were taken from a mixture containing 85·80 mg of niobium pentoxide, 7·30 mg of tantalum pentoxide, 0·60 mg of tungsten trioxide, 1·60 mg of titanium dioxide and 46·40 mg of ferric oxide

Sample No.	1	2	3
Nb_2O_5 *plus* Ta_2O_5 present, mg	93·1	93·1	93·1
Residue after acid hydrolysis,* mg	93·5	93·1	94·2
Residue after purification (Nb_2O_5 *plus* Ta_2O_5), mg	92·3	91·7	91·6
Nb_2O_5 found in purified residue by proposed method, mg	—	84·6, 84·3†	84·4, 83·8†
Nb_2O_5 found corrected for 93·1 mg of residue,‡ mg	—	85·9, 85·6	85·8, 85·2
Ta_2O_5 in purified residue (by difference), mg	—	7·1, 7·4†	7·2, 7·8†
Ta_2O_5 (by difference) corrected for 93·1 mg of residue,‡ mg	—	7·5	7·9

* Weight of residue after removal of silica by treatment with sulphuric and hydrofluoric acids.
† Average values of duplicate determinations.
‡ The weight of Nb_2O_5 *plus* Ta_2O_5 originally present.

The purified residue obtained from sample No. 1 was examined for contamination by titanium; chromotropic acid[6] was used after the residue had been fused in potassium hydrogen sulphate and the melt extracted with tartaric acid solution. The amount of titanium present was insignificant.

It can be seen that the weights of the purified residues obtained by the hydrolysis technique were slightly low, but the determination of niobium pentoxide in the prepared mixture by the proposed volumetric method was quantitative when the slight loss of niobium and tantalum during the purification was taken into account.

The method was next applied to the determination of niobium and tantalum in two alloys having the compositions shown below.

Element	Nb	Ta	W	Ti	Al	Co	Cr	Fe
Content in alloy No. 1, %	59·1	5·9	0·45	1·20	18·0	—	—	Base
Content in alloy No. 2, %	<3·0		11·0	—	—	Base	21·0	1·80

Alloy No. 1 was supplied and standardised by The London and Scandinavian Metallurgical Co. Ltd., and alloy No. 2 was supplied by Jessop Saville Ltd., Sheffield. The results obtained by the proposed procedure are shown in Table VI.

TABLE VI

NIOBIUM AND TANTALUM CONTENTS FOUND IN ALLOYS

Alloy No.	1	2
Nominal niobium content, %	59·1	<3·0
Nominal tantalum content, %	5·9	
Niobium content found, %	58·3, 58·6*	2·00, 2·01*
Tantalum content found, %	6·15, 6·35	0·66, 0·72

* Average results of duplicate determinations on separate samples.

The results for the ferro-niobium-tantalum alloy were slightly lower than expected. However, the results obtained from the analysis of the prepared mixture of oxides (Table V), which had a composition identical with that of the ferro-niobium-tantalum alloy, showed that slight loss of earth acids occurred during the magnesia purification process; when this loss was corrected for, recovery of niobium and tantalum was quantitative. Similar correction applied to the ferro-niobium-tantalum alloy gave results in good agreement with the nominal composition. The corrected results were 58·9 and 59·2 per cent. of niobium and 6·2 and 6·4 per cent. of tantalum.

Discussion of the method

The work described here shows that the quantitative reduction of niobium^{V} to niobium^{III} is possible. The inability of past workers to obtain quantitative reduction was due, in our opinion, to the use of unsuitable complexing agents, which resulted in formation of a non-reducible colloidal phase of niobium^{V}, and also the lack of appreciation that the niobium^{III} species is rapidly oxidised by hydrogen ion. The rate at which this oxidation occurs is shown in Fig. 1. The consistent but slightly low recoveries (96·5 ± 0·1 per cent.) in initial experiments with a delivery tube can be readily explained in terms of this effect.

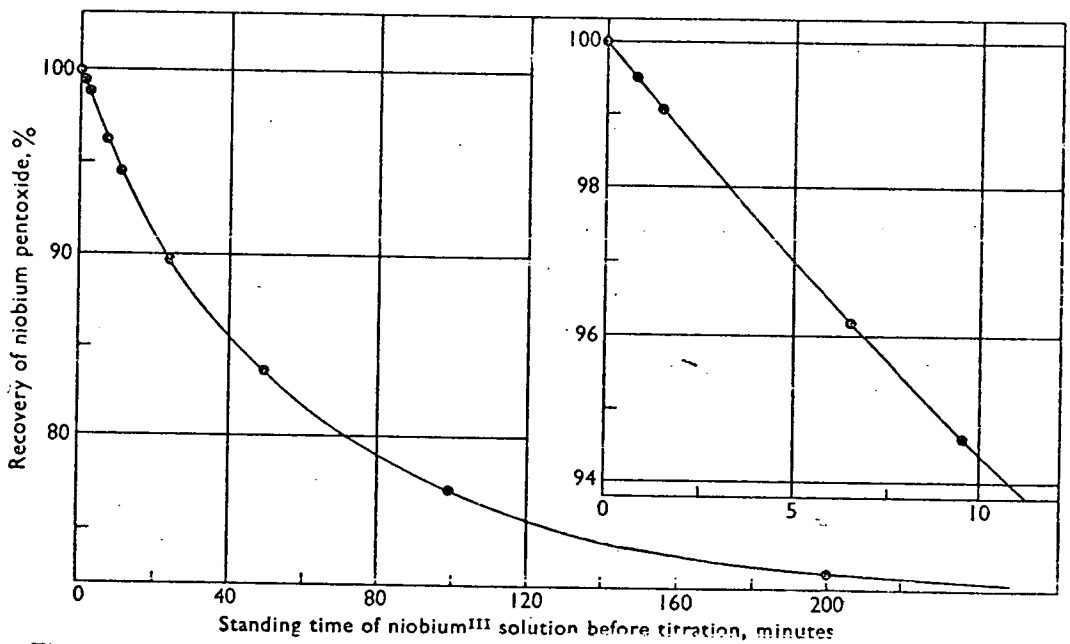

Fig. 1. Recovery - time curve for approximately 20-mg amounts of niobium^{III} in 6 M hydrochloric - 0·5 M hydrofluoric acid solution

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5

The Volumetric Determination of Iron, Molybdenum and Tungsten in Fluoride Solutions

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Both tungsten^{VI} and molybdenum^{VI} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid are quantitatively reduced to the tervalent state on a Jones reductor amalgamated to the extent of 0·75 per cent. w/w. They are determined, after collection in ammonium ferric sulphate solution, by titration with standard dichromate solution with barium diphenylamine sulphonate as indicator. Neither molybdenum^{VI} nor tungsten^{VI} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid is at all reduced on a silver reductor at 10° C, although iron^{III} is quantitatively reduced to iron^{II} under these conditions.

At 60° C in 0·2 M hydrofluoric acid - 1·5 to 2·0 M hydrochloric acid, molybdenum^{VI} is reduced quantitatively to molybdenum^{V} and in 0·2 M hydrofluoric acid - > 4 M hydrochloric acid quantitatively to molybdenum^{III}. No reduction of tungsten^{VI} in 0·2 M hydrofluoric acid - hydrochloric acid occurs on a hot silver reductor at a hydrochloric acid concentration below 5·5 M.

Solutions containing iron^{III}, molybdenum^{VI} and tungsten^{VI} and no other species capable of reduction have, therefore, been analysed for all three metals by using the Jones and silver reductors.

The methods have been applied to the analysis of synthetic mixtures, a standard ferro-molybdenum alloy and a standard ferro-tungsten alloy. The mean determined compositions for the molybdenum and tungsten contents of the alloys were identical to the certificate compositions. The maximum deviation of any result from the mean determined compositions was 0·2 per cent.

It has already been reported[1] that tungsten^{VI} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid is quantitatively reduced to tungsten^{III} on passage through a Jones reductor (38 cm long, 1·8 cm internal diameter, packed with 16- to 30-mesh zinc shot amalgamated to the extent of 0·75 per cent. w/w). The tungsten^{III} solution was collected in ammonium ferric sulphate solution under oxygen-free nitrogen, and the equivalent amount of iron^{II} thus produced was titrated with standard potassium dichromate solution in the presence of phosphoric acid with barium diphenylamine sulphonate as indicator. Up to 18·4 mg of tungsten trioxide were determined with a mean error for 16 determinations of —0·00(3) mg and a standard deviation from the mean error of 0·02(1) mg.

For amounts of tungsten trioxide in excess of 18·4 mg the reduction is not quantitative. This incomplete reduction is certainly associated with the fact that the tungsten^{III} species is fairly rapidly oxidised by hydrogen ion.[1] In an effort to extend the upper limit for quantitative reduction of tungsten^{VI}, the effect of different degrees of amalgamation of the zinc was investigated. A plot of oxidation state of the tungsten in the effluent from the reductor against amount of tungsten trioxide taken is shown in Fig. 1.

It is obvious that an amalgamation of 0·75 per cent. w/w, which was originally chosen, produces the most satisfactory conditions for reduction.

As expected, iron^{III} and molybdenum^{VI} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid are quantitatively reduced to iron^{II} and molybdenum^{III} under the same conditions as used for tungsten^{VI}. Up to 15·7 mg of iron^{III} were determined with a mean error for 11 determinations of —0·00(3) mg and a standard deviation from the mean error of 0·02(0) mg.

Up to 20·3 mg of molybdenum trioxide were determined with a mean error for 13 determinations of —0·00(5) mg and a standard deviation from the mean error of 0·01(8) mg.[1] In view of the fact that molybdenum^{III}, in contrast to tungsten^{III}, is much less rapidly oxidised by hydrogen ion,[1] it was surprising to find that the upper limit for the quantitative determination of molybdenum trioxide was 20·3 mg. On further investigation, it was ascertained that low results for amounts of molybdenum trioxide in excess of 20·3 mg were caused not by incomplete reduction to molybdenum^{III}, but by premature end-points in the

subsequent titration. Molybdenum^{III} from the reductor reacts with iron^{III} in the collecting vessel to produce iron^{II} and molybdenum^{V}. The iron^{II} reacts rapidly with dichromate in the titration, but molybdenum^{V} reacts only sluggishly, and a premature end-point is obtained for amounts of molybdenum trioxide in excess of 20·3 mg. For these larger amounts of molybdenum the indicator is oxidised before all of the molybdenum^{V} is titrated. By using the E.E.L. titrator with an Ilford No. 601 filter for photometric end-point detection, it was established that the molybdenum^{VI} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid is, in fact, quantitatively reduced to molybdenum^{III} for amounts up to at least 50·8 mg. The photometric titrations of iron^{II} *plus* molybdenum^{V} were made with standard dichromate solution in the absence of indicator. The end-point occurred at the intersection of two extrapolated straight lines on the plot of relative optical density against volume of titrant added, but the fact that the galvanometer needle took some time to fall to a steady value in the vicinity of the end-point verified that the reaction between molybdenum^{V} and dichromate was indeed slow.

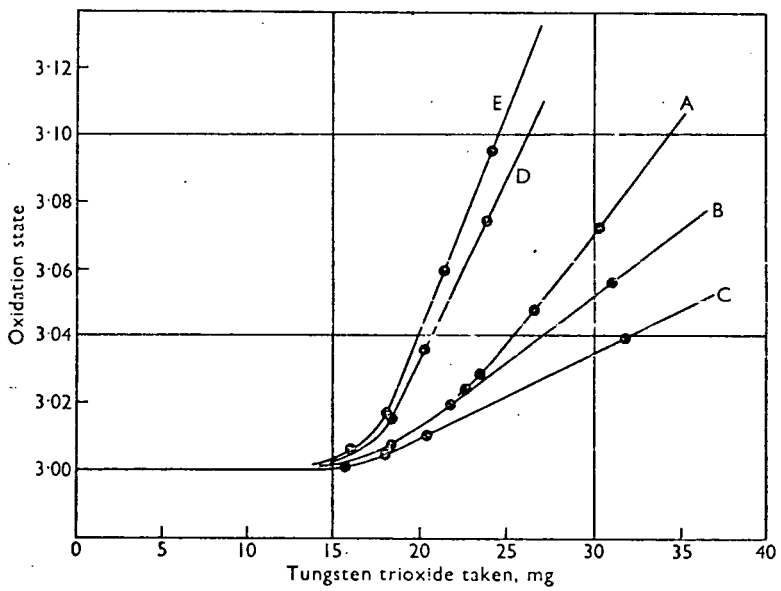

Fig. 1. Oxidation state of tungsten in the effluent from the Jones reductor as a function of the weight of tungsten trioxide taken for degrees of amalgamation of: curve A, 0·1 per cent. w/w; curve B, 0·5 per cent. w/w; curve C, 0·75 per cent. w/w; curve D, 1·0 per cent. w/w; curve E, 1·5 per cent. w/w

Although amounts of molybdenum trioxide between 20·3 and 50·8 mg could certainly be determined quantitatively by photometric titration, the method is not recommended because it is much slower than a visual titration. Conditions are easily arranged so that no more than 15 to 20 mg of molybdenum trioxide are passed through the reductor.

Incidentally, the low recoveries for amounts of tungsten trioxide in excess of 18·4 mg are associated with the side-reaction of tungsten^{III} and hydrogen ion in the reductor, and not with the titration. A photometric titration with dichromate of amounts of tungsten trioxide in excess of 18·4 mg after reduction and collection in iron^{III} solution, and in the absence of indicator, also produced low results. Iron^{III} and tungsten^{III} appear to react to give iron^{II} and tungsten^{VI}, and iron^{II} is titrated quantitatively with dichromate before the indicator is oxidised.

Although the method described above for the volumetric determination of tungsten is completely satisfactory, tungsten is often associated with iron and molybdenum, and it was felt that the full potentialities of the method would only be realised if suitable volumetric procedures that would lead to a quantitative determination of all three elements in mixtures could be developed.

It was therefore decided to investigate the reduction of iron^{III}, molybdenum^{VI} and tungsten^{VI} in fluoride solutions, on the silver reductor. It was soon established that iron^{III} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid, at about 10° C, is quantitatively reduced to iron^{II} on the silver reductor, whereas molybdenum^{VI} and tungsten^{VI} are unaffected. The reduced solution was again collected in ammonium ferric sulphate solution under nitrogen, and the iron^{II} was titrated with dichromate in the presence of phosphoric acid and barium diphenylamine sulphonate. Up to 22·0 mg of iron^{III}, alone and in the presence of molybdenum^{VI} and tungsten^{VI}, have been determined with a maximum error of 0·04 mg.

The fact that molybdenum^{VI} is not reduced at all in this medium is of considerable interest, because molybdenum^{VI} in 2 M hydrochloric acid is partly reduced to molybdenum^{V} at about 10° C on passage through the silver reductor (extent of reduction approximately 55 per cent.). It is evident that the molybdenum^{VI} is stabilised in the presence of hydrofluoric acid and is less easily reduced. Molybdenum^{VI} can, of course, be reduced quantitatively in solutions of 2 M hydrochloric acid at 60° to 80° C on passage through a silver reductor,[2]

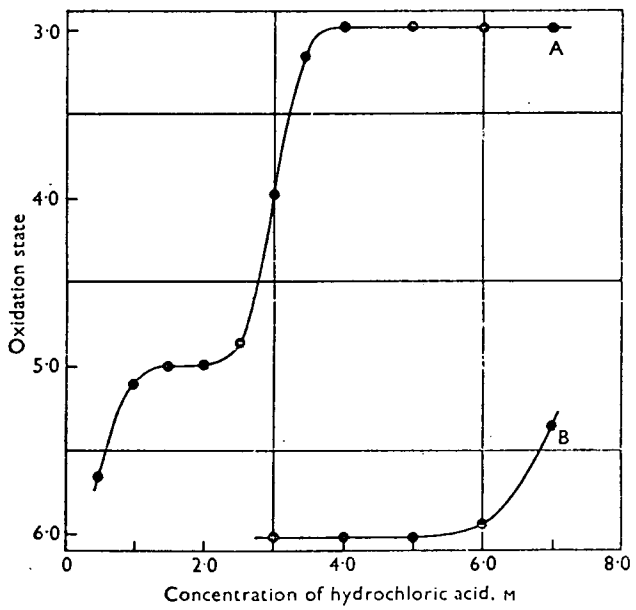

Fig. 2. Oxidation state of molybdenum and tungsten in the effluent from the hot silver reductor as a function of hydrochloric acid concentration: curve A, molybdenum; curve B, tungsten. The effluent was also 0·2 M in hydrofluoric acid.

and experiments were undertaken with a hot silver reductor to see if molybdenum^{VI} in hydrochloric - hydrofluoric acid solutions could be reduced to a definite oxidation state. Because hydrofluoric acid inhibits the reduction of molybdenum^{VI}, the concentration of this acid was reduced to 0·2 M, which is still sufficient to retain tungsten^{VI} in true solution. The extents of reduction of both molybdenum^{VI} and tungsten^{VI} in 0·2 M hydrofluoric acid containing 0·5 to 7 M hydrochloric acid are shown in Fig. 2.

As can be seen, molybdenum^{VI} is quantitatively reduced to molybdenum^{V} in 0·2 M hydrofluoric acid - 1·5 to 2·0 M hydrochloric acid, and to molybdenum^{III} in 0·2 M hydrofluoric acid - >4 M hydrochloric acid. Tungsten^{VI} is not reduced until the hydrochloric acid concentration exceeds 5·5 M.

By using synthetic solutions, it was established that up to 13·2 mg of molybdenum trioxide in 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid, both in the presence and absence of tungsten^{VI}, could be determined on the hot silver reductor with a maximum error of 0·04 mg. Iron^{III}, as expected, is quantitatively reduced to iron^{II} under these conditions.

The scheme outlined below is, therefore, available for determining mixtures of iron^{III}, molybdenum^{VI} and tungsten^{VI}. Iron^{III}, alone, is reduced on the cold silver reductor in 2 M hydrochloric acid - 0·5 M hydrofluoric acid. Iron^{III} and molybdenum^{VI} are reduced

together on the hot silver reductor in 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid. Iron^{III}, molybdenum^{VI} and tungsten^{VI} are all quantitatively reduced on the Jones reductor in 2 M hydrochloric acid - 0·5 M hydrofluoric acid. The results obtained for the analysis of synthetic mixtures of iron^{III}, molybdenum^{VI} and tungsten^{VI}, a ferro-molybdenum alloy and a ferro-tungsten alloy are reported below.

METHOD

APPARATUS—

Because of the corrosive nature of hydrofluoric acid solutions towards glassware, the apparatus used was constructed entirely in polythene.

The Jones reductor was prepared from heavy-gauge polythene tubing (length 38 cm; internal diameter 1·80 cm) narrowing rapidly at the base to a short piece of narrow-bore tubing, 4 mm in diameter. A polythene funnel 1½ inches in diameter at the maximum width, welded to the base of the reductor, served this purpose. The zinc shot was supported by a perforated disc of diameter 6 mm made from ⅛-inch polythene sheet and inserted into the wider end of the polythene funnel stem.

Polythene tubing (6 mm bore) was wrapped round the column from top to bottom in the form of a spiral, for cooling purposes. The collecting vessel was a 250-ml polythene bottle fitted with a polythene screw-cap having three holes in the top to accommodate the column delivery tube, and inlet and outlet tubes for nitrogen. The inlet tube reaches almost to the bottom of the bottle. A solution reservoir at the top of the reductor was made by welding a polythene funnel (3½ inches in diameter at the maximum width), from which the stem had been removed at the appropriate position, on to the top of the column. A screw-clamp at the base of the reductor prevented leakage when the column was not in use. The column of amalgamated zinc was 38 cm long.

The silver reductor was prepared from polythene tubing (length 38 cm; internal diameter 1·0 cm) narrowing rapidly at the base to a short piece of narrow-bore tubing, 5 mm in diameter, just long enough to protrude into the collecting vessel. The central portion (28 cm long) of the reductor tube was encased in heavy-gauge polythene tubing (1·8 cm internal diameter) sealed on to the reductor at each end, with an inlet tube at the bottom and an outlet tube at the top, in the form of a Liebig condenser. This permitted the temperature of the reductor to be controlled as required. The solution reservoir at the top of the reductor, the perforated disc for supporting the silver, and the collecting bottle were constructed and fitted to the column as for the Jones reductor. The column of silver was 34 cm long.

REAGENTS—

Hydrofluoric acid and other acids—These were of analytical-reagent grade.

Nitrogen—This was oxygen-free "spot" nitrogen obtained from the British Oxygen Co. Ltd.

Potassium dichromate solution—An exactly 0·1000 N (M/60) solution of potassium dichromate was prepared from the analytical-reagent grade salt.

Oxygen-free distilled water—This was prepared by boiling distilled water vigorously for 15 minutes and allowing it to cool under liquid paraffin. The water was stored under liquid paraffin.

Standard solutions of iron, molybdenum and tungsten—(1) *Iron*—This was prepared from AnalaR ammonium ferric sulphate that had been analysed for iron by using the usual gravimetric method of hydroxide precipitation, and then filtration and ignition to ferric oxide. (2) *Molybdenum and tungsten*—These were prepared from Specpure trioxides, obtained from Johnson, Matthey and Co. Ltd., by dissolving accurately weighed amounts of the trioxides in boiling ammonium hydroxide, sp.gr. 0·88, in 100-ml polytetrafluoroethylene beakers. When dissolution was complete the solutions were evaporated to dryness to remove the excess of ammonia. The resulting solids were dissolved by heating gently with 10 ml of a solution of diluted hydrofluoric acid (2 + 3), adjusted to be 0·5 M in hydrofluoric acid and stored in screw-cap polythene bottles. The concentration of the element was arranged to be approximately 3 to 4 mg per g of solution.

PREPARATION OF AMALGAMATED ZINC SHOT—

AnalaR zinc shot, 16 to 30 mesh (batch Nos. 53324 and 58066), was obtained from Hopkin and Williams Ltd. The zinc shot was amalgamated to the extent of 0·75 per cent. w/w by vigorously shaking 500 g of shot—previously washed with dilute hydrochloric acid

(2 + 98) and then with distilled water—with 250 ml of 2 per cent. w/v mercuric chloride solution in a stoppered flask for 45 to 60 seconds. The supernatant solution was discarded, and the shot was washed several times with distilled water and then once with dilute sulphuric acid (2 + 98). The shot was finally washed with distilled water and stored under dilute hydrochloric acid (1 + 99).

Zinc shot amalgamated to the extent of 0·1 per cent., 0·5 per cent., 1·0 per cent. or 1·5 per cent. w/w was prepared in the same way by shaking, in each instance, 500 g of shot with the appropriate amount of mercuric chloride solution.

PREPARATION OF SILVER FOR THE SILVER REDUCTOR—

The silver was prepared from AnalaR silver nitrate by dissolving 40 g of the salt in 250 ml of distilled water containing 5 ml of nitric acid, sp.gr. 1·42. This solution was then agitated with a sheet of electrolytic copper until deposition of the silver was complete. The precipitated silver was washed thoroughly with dilute sulphuric acid (1 + 99) until free from copper^{II} ions, and then with distilled water until free from sulphuric acid. The silver was stored under dilute hydrochloric acid (1 + 99).

PREPARATION OF THE FERRO ALLOYS FOR ANALYSIS—

Dissolve 0·1 to 0·2 g of alloy in 5 ml of 40 per cent. w/w hydrofluoric acid and 1 ml of 36 per cent. w/w hydrochloric acid in a 100-ml polytetrafluoroethylene beaker. Add 1 ml of 100-volume hydrogen peroxide, and heat gently until dissolution is complete.

Evaporate the solution gently to dryness, and redissolve the solid in 5 ml of 40 per cent. w/w hydrofluoric acid. Repeat this operation twice to destroy excess of hydrogen peroxide. Redissolve the solid in 5 ml of diluted hydrofluoric acid (2 + 3), and transfer the solution to a dry, pre-weighed, 100-ml polythene bottle fitted with a polythene screw-cap, washing the beaker several times with oxygen-free distilled water. Transfer the washings to the bottle.

Place 5 ml of dilute hydrofluoric acid (1 + 10) in the beaker, and boil gently for a few minutes. Transfer the solution and subsequent beaker washings to the bottle, and dilute to a suitable volume with oxygen-free distilled water. Cool the bottle and solution to room temperature, and re-weigh.

PROCEDURES FOR DETERMINING IRON^{III}, MOLYBDENUM^{VI} AND TUNGSTEN^{VI}—

(*a*) *Iron*—Transfer a suitable weighed portion of solution containing not more than 22·0 mg of iron to a 65-ml (2-oz) polythene bottle calibrated at 50 ml. Add sufficient 36 per cent. w/w hydrochloric acid and dilute hydrofluoric acid (1 + 9) so that the final composition of the solution, when diluted to 50 ml with oxygen-free distilled water, is 2·0 M in hydrochloric acid and 0·5 M in hydrofluoric acid. Dilute to the 50-ml mark.

Connect the water-jacket of the silver reductor to a cold-water tap, and allow water to pass through freely. Then open the screw clamp on the bottom of the reductor column. Allow the solution level inside the reductor to fall almost to the silver, and add 25 ml of 2 M hydrochloric acid - 0·5 M hydrofluoric acid wash solution to the reductor reservoir. Pass this solution through the reductor at a flow rate of 5 ml per minute. When the solution level again almost reaches the silver add a further 25-ml portion. Repeat this operation until 100 ml of wash solution have been passed through the reductor. At no time should the solution level fall below the level of the silver.

When the final 25-ml portion of wash solution has been added to the reservoir, start the flow of nitrogen to the inlet tube of the collecting bottle, and adjust the flow-rate to approximately 250 ml per minute.

Immediately before the level of solution in the reductor reaches the silver, attach to the base of the column a 250-ml polythene bottle containing 10 ml of 0·1 M ammonium ferric sulphate solution and 30 ml of phosphoric acid, sp.gr. 1·75.

Introduce the iron^{III} solution into the top of the column in 5- to 10-ml portions, and maintain a constant depth of solution above the silver. Take 50 ml of 2 M hydrochloric acid - 0·5 M hydrofluoric acid wash solution, and rinse the 2-oz polythene bottle with three 5-ml portions. Pour these rinsings on to the column, allowing the level of solution in the column to fall almost to the level of the silver before adding the next portion. Add the remaining 35 ml of wash solution in a similar manner. When the level of the final 5-ml portion has almost reached the silver, unscrew the collecting vessel, and rinse the nitrogen-flow tube with oxygen-free distilled water during removal of the bottle.

Add 30 ml of phosphoric acid, sp.gr. 1·75 (see Note 1), and 10 ml of sulphuric acid, sp.gr. 1·84. Dilute the solution to 230 to 240 ml with oxygen-free distilled water. Add exactly 5 drops (0·25 ml) of an aqueous 0·2 per cent. w/v solution of barium diphenylamine sulphonate as indicator, and titrate the solution with 0·1000 N potassium dichromate to a permanent purple end-point. Add titrant from a 5- or 10-ml calibrated grade-A microburette. Subtract from the titre a blank value (see Note 2 (*i*)).

Process a duplicate portion of iron solution of approximately half or double the weight of the first portion.

1·000 ml of 0·1000 N potassium dichromate ≡ 5·585 mg of iron.

(*b*) *Iron and molybdenum*—Transfer a suitable weighed portion of solution containing not more than 22·0 mg of iron and 13·2 mg of molybdenum trioxide (8·8 mg of molybdenum) to a 65-ml (2-oz) polythene bottle calibrated at 50 ml. Add sufficient 36 per cent. w/w hydrochloric acid and dilute hydrofluoric acid (1 + 49) so that the final composition of the solution, when diluted to 50 ml, is 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid. Dilute the solution to approximately 40 ml with distilled water, and pass a steady stream of oxygen-free nitrogen through it for 15 minutes (see Note 2 (*ii*)). Rinse the nitrogen-flow tube with oxygen-free distilled water during removal of the bottle, and dilute the solution to the 50-ml mark.

Connect the water-jacket of the silver reductor to a supply of water at 70° C (see Note 3), and allow the temperature of the reductor to become constant. Then open the screw-clamp at the base of the reductor. When the level of solution in the reductor column has almost fallen to the silver, add 25 ml of 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid wash solution, and wash the column in the same way as with the iron solution in procedure (*a*), but use 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid wash solution.

When the final 25-ml portion of wash solution has been added to the reservoir, heat the sample solution by immersing its container in a small reservoir into which is flowing the waste water from the reductor heater. The reservoir was constructed from a 250-ml polythene bottle, from which the top part had been removed at the appropriate position. A side-arm was fitted to the reservoir ¼ inch from the top as an overflow pipe.

When the level of the final 25-ml portion of wash solution has fallen almost to the level of the silver, attach a collecting bottle containing 10 ml of 0·1 M ammonium ferric sulphate solution and 30 ml of phosphoric acid, sp.gr. 1·75, to the base of the reductor. Introduce the hot solution containing the iron and molybdenum into the top of the reductor in 5- to 10-ml portions, and process as in procedure (*a*), but use 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid wash solution.

Rinse the nitrogen-flow tube with oxygen-free distilled water during the removal of the collecting bottle. Add 30 ml of phosphoric acid, sp.gr. 1·75 (see Note 1), and dilute the solution to 230 to 240 ml with oxygen-free distilled water. Add indicator, and titrate the solution as in procedure (*a*). Subtract from the titre a blank value (see Note 2 (*ii*)) and a volume of 0·1000 N potassium dichromate equivalent to the amount of iron present in the portion.

Process a duplicate portion of approximately half or double the weight of the first.

1·000 ml of 0·1000 N potassium dichromate
≡ 4·798 mg of molybdenum trioxide
≡ 3·198 mg of molybdenum.

(*c*) *Iron, molybdenum and tungsten*—Transfer a suitable weighed portion of solution containing not more than 15·7 mg of iron, 20·3 mg of molybdenum trioxide (13·5 mg of molybdenum) and 18·4 mg of tungsten trioxide (14·6 mg of tungsten) to a 65-ml (2-oz) polythene bottle calibrated at 50 ml. Add sufficient 36 per cent. w/w hydrochloric acid and dilute hydrofluoric acid (1 + 9) so that the final composition of the solution, when diluted to 50 ml with oxygen-free distilled water, is 2 M hydrochloric acid - 0·5 M hydrofluoric acid. Dilute to the 50-ml mark.

Connect the cooling-spiral of the Jones reductor to a cold-water tap, and run the water for some minutes. Then open the screw-clamp at the base of the reductor. Drain the solution in the column until the level almost reaches the zinc shot, and wash the column with four 25-ml portions of 2 M hydrochloric acid - 0·5 M hydrofluoric acid wash solution.

Process the sample solution in exactly the same way as described in procedure (*a*), but use 35 ml of wash solution instead of 50 ml to wash the sample solution through the reductor.

Rinse the nitrogen-flow tube with oxygen-free distilled water during removal of the collecting vessel.

Add 30 ml of phosphoric acid, sp.gr. 1·75 (see Note 1), and 10 ml of sulphuric acid, sp.gr. 1·84. Dilute the solution to 230 to 240 ml with oxygen-free distilled water. Add indicator solution, and titrate exactly as in procedure (*a*).

Subtract from the titre a blank value (see Note 2 (*iii*)) and calculated volumes of 0·1000 N potassium dichromate equivalent to the amounts of iron and molybdenum present in the portion of sample solution.

1·000 ml of 0·1000 N potassium dichromate
≡ 7·730 mg of tungsten trioxide
≡ 6·131 mg of tungsten.

Notes

1. Interference from tungsten^{VI}—

It has already been reported[3] that the end-point as shown by the colour change of barium diphenylamine sulphonate indicator in the titration of iron^{II} with potassium dichromate solution, is retarded in the presence of chloride ion. This effect increases with increasing concentration of chloride ion in the titrand, but is constant for a fixed concentration of chloride ion. The chloride ion concentration is therefore partly responsible for the magnitude of the blank value.

However, the blank value was found to vary when iron^{II}, in the presence of a fixed concentration of chloride ion but increasing amounts of tungsten^{VI}, was titrated with potassium dichromate with barium diphenylamine sulphonate as indicator. The blank value decreased as the concentration of tungsten^{VI} increased. Tungsten^{VI} appears to have a catalytic effect on the colour change of the indicator. Why chloride ion and tungsten^{VI} should influence the oxidation mechanism of the indicator is not obvious, but the variable effect produced by different amounts of tungsten^{VI} can be overcome by adding 30 ml of phosphoric acid, sp.gr. 1·75 (making 60 ml in all), before titrating the iron^{II} with dichromate. Under these conditions the blank value is constant in the presence of a fixed amount of chloride ion and 0 to 60 mg of tungsten trioxide.

2. Determination of blank values—

(*i*) *The cold silver reductor*—There are four sources of error, three positive and one negative. These are (*a*) impurities present in the reagents, (*b*) chloride ion concentration, (*c*) theoretical indicator blank value—all positive effects—and (*d*) hydrogen peroxide produced in the silver reductor[4] by reduction of dissolved oxygen present in the solutions—a negative effect. The positive effects are constant for a fixed chloride ion concentration, but the negative effect may differ from one solution to another according to oxygen content.

Because a sample solution, whose iron content is to be determined, may have a different oxygen content from that of a standard iron solution, it is not advisable to apply to the sample solution a correction for a blank value determined for a standard solution. The blank value should be obtained by processing two portions of sample solution, which should be fairly different in weight, and applying the equation—

$$b = \frac{W_1V_2 - W_2V_1}{W_1 - W_2}$$

where b is the blank value in millilitres, W_1 and W_2 are weights of sample solution taken and V_1 and V_2 are the titres in millilitres for W_1 and W_2, respectively.

(*ii*) *The hot silver reductor*—Although the blank value is reasonably constant for various amounts of standard iron^{III} solution passed through a cold silver reductor, this is not so for a hot silver reductor. The blank value is generally lower, presumably because more hydrogen peroxide is produced, and is more variable. Since different portions of a sample solution, after adjustment to a volume of 50 ml with hydrochloric and hydrofluoric acids, are unlikely to have identical oxygen contents, it was considered advisable to remove the oxygen from these solutions by passing oxygen-free nitrogen through them for 15 minutes before processing them on the reductor.

Various amounts of iron^{III} solution, which had been gassed out with nitrogen and passed through the hot reductor, showed, as expected, a higher and much more consistent blank value.

The blank values are again determined by using the equation shown in Note 2 (*i*).

(*iii*) *The Jones reductor*—No difficulty from hydrogen peroxide is encountered in using the Jones reductor, since any oxygen present in the solution being passed through the reductor is completely reduced to water.[5] To determine the blank value for the Jones reductor, process a series of various standard amounts of iron^{III} in 2 M hydrochloric acid - 0·5 M hydrofluoric acid. (Molybdenum^{VI} or tungsten^{VI} can also be used, but iron^{III} is cheapest.) In each determination calculate the volume of 0·1000 N potassium dichromate theoretically required to titrate the iron^{II} produced by the reductor, and subtract this volume from the experimental titre. None of the blank values should differ from the mean blank value by more than 0·004 ml.

A typical blank value for the Jones reductor for an iron^{III} solution was 0·105 ml.

3. HOT WATER SUPPLY—

The temperature of the water supply to the silver reductor was maintained at 70° C by passing warm water at 40° C through two Liebig condensers connected in series, up the centre of which steam was passing. The temperature of the water supply to the reductor could then be adjusted by altering either the rate of flow of the water or the pressure of steam. The fall in temperature from the bottom to the top of the reductor column is 3° to 4° C.

The temperature of the effluent containing the reduced species under these conditions is 58° to 60° C.

RESULTS

TABLE I

ANALYSIS OF SOLUTIONS OF PREPARED MIXTURES OF IRON, MOLYBDENUM AND TUNGSTEN

Solution number	Iron content		Molybdenum trioxide content		Tungsten trioxide content	
	Actual, mg	Determined, mg	Actual, mg	Determined, mg	Actual, mg	Determined, mg
1	32·5	32·6	74·2	74·2	20·5	20·6
2	30·6	30·6	30·9	30·7	73·4	73·5
3	46·2	46·2	47·7	47·8	52·3	52·3
4	68·0	68·1	35·8	35·9	74·1	74·0
5	63·1	63·0	74·7	74·9	18·2	18·2

Solutions were prepared from stock solutions of the three elements; the total weight of each solution was approximately 30 g. Suitable fractions were analysed by the methods described above, and the results are shown in Table I.

TABLE II

RESULTS FOR THE ANALYSIS OF FERRO ALLOYS

Alloy			Determined composition		
B.C.S. number	Certificate composition, %	Sample number	Iron, %	Molybdenum, %	Tungsten, %
231/2	Molybdenum 70·1	1	28·8, 28·9	70·2, 70·0, 70·2,* 70·0,* 69·9,* 70·2*	—
		2	28·9, 29·0	70·0, 70·0, 70·1,* 70·2,* 69·9*	—
242/1	Tungsten 82·0	1	17·5, 17·5	0·3(2), 0·3(2)	82·0, 82·0
		2	17·4, 17·6	0·5(5), 0·5(5)	82·0, 81·9

* Obtained by using the Jones reductor; the other molybdenum values were obtained by using the silver reductor.

DISCUSSION

Although the maximum amount of molybdenum^{VI} in 4·5 M hydrochloric acid - 0·2 M hydrofluoric acid, determined by using the hot silver reductor, was 13·2 mg expressed as molybdenum trioxide (8·8 mg of molybdenum), it is extremely likely that, as with the Jones reductor, amounts of molybdenum trioxide up to 20·3 mg (13·5 mg of molybdenum) could be determined, by using a visual titration with potassium dichromate solution and barium diphenylamine sulphonate as indicator.

The maximum amount of iron^{III} determined in 2 M hydrochloric acid - 0·5 M hydrofluoric acid by using the Jones reductor was 15·7 mg, but much larger amounts are likely to be quantitatively reduced on this reductor.

It is evident from Table II that the methods just described should be useful for determining iron, molybdenum and tungsten in ferro-molybdenum, ferro-tungsten and certain other alloys, preferably after a qualitative spectrographic analysis to make absolutely certain that the alloys contain no appreciable amounts of other elements that could interfere in the methods by being reduced on the silver or Jones reductors.

The behaviour of a few elements that can be quantitatively reduced to lower oxidation states on metal reductors from solutions free from fluoride was investigated for the fluoride systems employed for iron, molybdenum and tungsten. In all instances the maximum amount of element passed through the reductor was 14·3 mg. The procedures used for the reductions and titrations were identical to those employed for iron, molybdenum and tungsten. The results are shown in Table III.

TABLE III

OXIDATION STATES OF VANADIUM, TITANIUM AND CHROMIUM AFTER PASSAGE THROUGH VARIOUS REDUCTORS

Species	Oxidation states of the species in the effluent from the reductor		
	Cold silver	Hot silver	Jones
Vanadium^{V}	+4·00	+4·00	+2·00
Titanium^{IV}	+4·00	+4·00	+3·00
Chromium^{III}	+3·00	+3·00	+2·83

Chromium^{III} is not reduced to a definite oxidation state on the Jones reductor in cold 2 M hydrochloric acid - 0·5 M hydrofluoric acid.

Vanadium^{IV} reacts with iron^{III} in the collecting vessel to produce iron^{II} and vanadium^{IV}. In the titration of such a solution with barium diphenylamine sulphonate as indicator, the indicator changes colour before any of the vanadium^{IV} is oxidised. Vanadium^{IV} can, however, be determined by photometric titration with dichromate in the absence of the indicator.

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THE VOLUMETRIC DETERMINATION OF MANGANESE IN FLUORIDE SOLUTIONS WITH PARTICULAR REFERENCE TO THE ANALYSIS OF ALLOYS

IT has already been reported[1] that manganese^{II} in 0·5 M hydrofluoric acid - 0·5 M ammonium fluoride solution is quantitatively oxidised to a manganese^{III} fluoride complex by permanganate and that this reaction can be employed for the volumetric determination of maganese^{II} when the end-point is detected photometrically. Except for obvious reducing agents, it was considered that only cobalt^{II}, nickel^{II}, copper^{II} and chromium^{III} in fluoride solutions could possibly be oxidised to higher oxidation states by permanganate, but it was soon established that these species, in the presence or absence of manganese^{II}, were not, in fact, oxidised by permanganate. There was also no interference from small amounts of nitrate or sulphate. The reaction therefore seems to be selective for manganese^{II} in the presence of other elements.

Manganese^{II} in 0·5 M hydrofluoric acid - 0·5 M ammonium fluoride solutions can be titrated with permanganate visually, provided that the solution to be titrated is colourless. The manganese^{III} fluoride complex is pale orange-brown in colour, but the merest excess of permanganate can readily be detected by eye, after a little practice, when the titrand contains up to at least 15 mg of manganese^{II} per 100 ml. Under these conditions, 2·5 to 15 mg of manganese^{II} in 100 ml of solution were determined with a mean error for 19 determinations of 0·00(1) mg and a standard deviation from the mean error of 0·02(0) mg.

On the other hand, it is much more difficult to obtain accurate results when manganese^{II}, in the presence of coloured ions, is titrated visually with permanganate, and in these instances a photometric titration should be carried out. Two- to ten-milligram amounts of manganese^{II} in 30 ml of 0·5 M hydrofluoric acid - 0·5 M ammonium fluoride solution containing 4- to 12-mg amounts of cobalt^{II}, nickel^{II}, copper^{II} and chromium^{III}, individually or in combination, were titrated photometrically with a mean error for 11 determinations of −0·00(4) mg and a standard deviation from the mean error of 0·01(4) mg.

METHOD

REAGENTS—

Potassium permanganate solution, approximately 0·02 M—The solution is standardised against sodium oxalate of analytical-reagent grade.

1 ml of 0·02 M potassium permanganate ≡ 4·394 mg of manganese^{II}.

All other reagents must be of analytical-grade.

APPARATUS—

E.E.L. Titrator (for the photometric titrations)—The titration cell, capacity 50 ml, was constructed from Perspex tube and sheet.

PROCEDURE FOR ANALYSING ALLOYS CONTAINING 2 PER CENT. OR MORE OF MANGANESE—

Dissolve 0·1 to 0·25 g of alloy in 20 ml of concentrated hydrochloric acid *plus* 10 ml of concentrated nitric acid in a beaker. Add 2·5 ml of concentrated sulphuric acid, and evaporate the solution to fumes of sulphur trioxide. Cool the beaker and contents. If the alloy contains vanadium, add, dropwise, a solution of potassium dichromate (approximately 0·5 per cent. w/v) until a slight excess is present (see Note 1). Heat the solution to about 95° C, cool to room temperature, remove any precipitate of hydrated tungstic oxide by spinning in a centrifuge, and dilute the solution to 25 ml in a calibrated flask.

Visual titration—Dispense a suitable aliquot of solution (1 to 5 ml containing 1 to 15 mg of manganese^{II}) by weight or volume into a 250-ml polythene bottle. Add calculated volumes of 5 M ammonium fluoride and 5 M hydrofluoric acid to give a final concentration of approximately 0·5 M hydrofluoric acid and 0·5 M ammonium fluoride. Dilute the solution to 100 ml, and titrate with standard permanganate solution to the first appearance of a permanent pink colour. Subtract a blank titre obtained under the same conditions.

Photometric titration—Dispense a suitable aliquot of solution (1 to 5 ml containing 1 to 15 mg of manganese^{II}) by weight or volume into the titration cell. Add calculated volumes of 5 M ammonium fluoride and 5 M hydrofluoric acid to give a final concentration of approximately 0·5 M ammonium fluoride and 0·5 M hydrofluoric acid. Dilute the solution to 30 ml, and titrate with standard permanganate solution in the E.E.L. Titrator with an Ilford No. 604 filter and an initial

relative optical-density reading of zero. Plot a graph of relative optical density, corrected for volume change, against volume of titrant added, and extrapolate the straight line portions of the graph to intersect at the end-point as shown in Fig. 1. Subtract a blank titre obtained under the same conditions.

PROCEDURE FOR ANALYSING ALLOYS CONTAINING LESS THAN 2 per cent. OF MANGANESE—

The procedure is essentially the same as that described above, but a sample weight of 0·25 to 1 g is taken, and 5 ml of concentrated sulphuric acid are added to the solution after the alloy has dissolved. A 5-ml aliquot of solution is taken from the calibrated flask for both visual and photometric titration. However, this aliquot of manganese^{II} solution contains too much sulphuric acid for it to be converted to 0·5 M hydrofluoric acid by the addition of reasonable volumes of 5 M ammonium fluoride and water, and it is therefore necessary to neutralise most of the sulphuric acid before adding ammonium fluoride and hydrofluoric acid. This is done by adding dilute ammonia solution (1 + 3) to the first appearance of a permanent precipitate and then immediately adding hydrofluoric acid and ammonium fluoride (see Note 2).

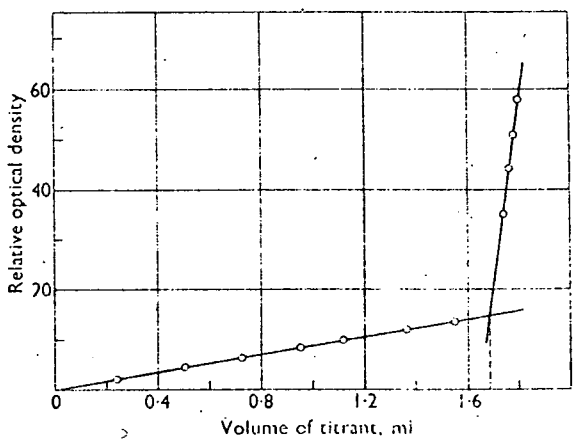

Fig. 1. Photometric titration of manganese^{II} in 9·3 mg of ferromanganese with 0·0200 M potassium permanganate

NOTES—

1. Vanadium^{IV} is incompletely oxidised to vanadium^{V} on treatment with aqua regia and sulphuric acid (10·4 mg of vanadium^{IV} was oxidised only to the extent of 67 per cent. with the use of these acids). However, the vanadium^{IV} remaining in the solution is readily oxidised by potassium dichromate. Dichromate does not oxidise manganese^{II} in cold fluoride solutions.

2. In the initial experiments, all the sulphuric acid solutions were neutralised with ammonia to the first appearance of a precipitate, but slightly low results were obtained for alloys containing large amounts of manganese. This was presumably due to the partial oxidation of manganese^{II} hydroxide to manganese^{III} hydroxide. For ferrous alloys containing less than 2 per cent. of manganese, no aerial oxidation of manganese^{II} occurred because the small amount of precipitate produced contained no manganese^{II} hydroxide and was essentially ferric hydroxide. In the analysis of non-ferrous alloys containing less than 2 per cent. of manganese, it is advisable to add 15 mg of iron^{III} to the solution before neutralisation to ensure that the precipitate produced contains no manganese^{II} hydroxide.

CONCLUSIONS

The method described above will offer no distinct advantage over the usual colorimetric method[2] for a manganese content in an alloy of less than 2 per cent. However, for larger amounts of manganese the method would appear to offer many advantages over well-established methods.[3,4] It should also compare favourably with the modified Lingane - Karplus method[5] in that a quick visual titration is possible for determining manganese in many alloys, if results of the highest precision are not required (see Table I).

TABLE I

RESULTS

Alloy	Manganese content, %	Sample No.	Manganese found by—visual titration, %	Manganese found by—photometric titration, %
Permanent magnet alloy B.C.S. No. 266	0·27	1	unsuitable	0·26, 0·27
		2		0·28, 0·28
High-speed steel B.C.S. No. 241	0·30	1	unsuitable	0·30, 0·31
		2		0·29, 0·29
13% manganese steel B.C.S. No. 290	12·9	1	12·83, 12·89, 12·98	12·90, 12·91
		2	12·88, 13·00	12·90, 12·91
Low-carbon ferromanganese B.C.S. No. 280	80·4	1	80·30, 80·34, 80·46	80·48, 80·50
		2	80·20, 80·30	80·42, 80·44

The total time for analysis of ferromanganese was 35 to 40 minutes by visual titration.

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Polarographic Investigation in Acidic Fluoride Solutions

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ABSTRACT

A study has been made of the polarographic behaviour of gallium, indium, thallium (I), tin (II) and (IV), lead, arsenic (III) and (V), antimony (III) and (V), bismuth, titanium (IV), zirconium, vanadium (IV), niobium (V), tantalum, chromium (III), molybdenum (VI), tungsten (VI), uranium (VI), manganese (II), rhenium (VII), iron (II) and (III), cobalt (II), nickel, copper (II), silver, zinc and cadmium in hydrofluoric acid–ammonium fluoride base electrolyte using a Sargent Model XV recording polarograph, Teflon dropping mercury electrodes and polythene cells. The polarographic reduction of molybdenum (VI) has also been investigated in hydrochloric acid–hydrofluoric acid and sulphuric acid–hydrofluoric acid base electrolytes.

Where appropriate, half-wave potentials obtained in fluoride solution are compared with those obtained in perchlorate base electrolyte in order to gain information about the complexing effects of fluoride ion.

The results, which have so far been obtained, indicate the possibility of determining polarographically, copper, bismuth, tin, lead, thallium, cadmium, molybdenum, iron, nickel and zinc in the presence of titanium, zirconium, niobium, tantalum and tungsten. Half-wave potentials of -0.228 V, -0.402 V and -0.602 V for the oxidation of tin (II), the reduction of lead and the reduction of tin (II) respectively in 0.1 *M* hydrofluoric acid–0.1 *M* ammonium fluoride, suggest a new method for the determination of tin and lead in alloys.

Recently it has been established that the reduction of niobium (V)[1] and

tungsten (VI)[2] to trivalent species is quantitative when these elements, dissolved in hydrochloric–hydrofluoric acid media, are passed through a Jones reductor. In the presence of hydrofluoric acid, the hydrolytic and polymeric reactions of niobium (V), tantalum (V) and tungsten (VI), which are so troublesome in most acidic solutions, are prevented, because fluoride forms very strong complexes with these elements.

It was therefore logical to examine the polarographic behaviour of these and other elements in fluoride solutions, with a view to developing new, fast methods of polarographic analysis for materials containing niobium, tantalum and tungsten.

Only a few papers have been published on polarography in fluoride media. The most detailed study made until now was by West and co-workers[3] who describe polarographic waves for eighteen metallic ions in acidic fluoride solutions. However, the results presented in that paper, and in others reporting polarographic studies with a D.M.E. in acidic fluoride solutions before 1962, are not entirely satisfactory, since all such investigations appear to have been carried out using glass capillaries as dropping mercury electrodes, and these are attacked by hydrofluoric acid. In 1962 a description of a Teflon dropping mercury electrode, which performs satisfactorily in glass-corroding media, was published,[4] but a detailed study of polarographic waves in acidic fluoride solutions using such an electrode has not yet been reported. Since the Teflon dropping mercury electrode was developed, Mesaric and Hume,[5,6] have measured polarographically the formation constants of lead-, copper-, cadmium-, and zinc-fluoride complexes using as dropping mercury electrode, a glass capillary coated with Tygon.

Apparatus and reagents

Polarograph. A Sargent Model XV polarograph was used.

Dropping Mercury Electrodes. These were constructed out of Teflon according to the method of Raaen.[4] Most polarograms were recorded using Teflon segments with orifices of 90 μ and 96 μ. A few polarograms were obtained using a Teflon segment with a 150 μ orifice. These segments were fitted to suitable lengths of Sargent 2–5 sec or 6–12 sec glass capillaries.

Polarographic Cells. For work in fluoride-free base electrolytes, Meites type H-cells (Sargent S-29396) were used with a S.C.E. in the reference electrode compartment. For studies in acidic fluoride solutions, H-cells were constructed out of polythene. A S.C.E. was again used as reference electrode. In a polythene cell the agar-salt bridge was supported against a perforated polythene disc fitted at the end of the

bridge nearest to the solution compartment. Complete details about the construction of these polythene cells are reported elsewhere.[7] In both types of cell the salt bridge consisted of saturated potassium chloride–4% agar (w/v) except when it was known that trace amounts of chloride would produce undesirable effects in the solution compartments. When this was so, saturated sodium fluoride or perchlorate solutions replaced the saturated potassium chloride solution in the salt bridge.

The resistances of both types of H-cell were approximately 300 Ω.

All polarographic cells were immersed in a water tank thermostated at 25.0°C: solutions were freed from dissolved oxygen by bubbling oxygen-free nitrogen.

Reagents. These were the purest available and were generally spectrographically pure or of analytical reagent grade. All fluoride solutions were stored in polythene bottles.

Results and discussion

Because the polarographic behaviour of several oxygenated species was to be examined, a buffer solution was required as base electrolyte and 0.1 *M* hydrofluoric acid–0.1 *M* ammonium fluoride was selected for this purpose. $E_{\frac{1}{4}}$ values and other information on the shapes of the polarographic waves of 24 elements in this base electrolyte are given in Table 1. This table also contains similar information for many of these elements in 0.1 *M* sodium perchlorate or 0.1 *M* perchloric acid. Some information on the complexing ability of fluoride ions for metals in 0.1 *M* hydrofluoric acid–0.1 *M* ammonium fluoride is thus provided.

It can be seen from the table that bismuth, tin (II), lead, thallium (I), cadmium and zinc produce, in fluoride solution, waves that are reversible or almost so. If i_d/C is a constant for these waves, and there is no reason to believe that it will not be so, then the polarographic determination of these elements in 0.1 *M* hydrofluoric acid–0.1 *M* ammonium fluoride will be straightforward. The waves for iron (III), molybdenum (VI), antimony (III) and nickel in the fluoride base electrolyte are irreversible, but they could probably be employed for the quantitative determination of these elements. The double wave for copper (II) starts immediately after the anodic oxidation of mercury, but diffusion current measurements made on the plateau might serve as a means for the quantitative determination of copper.

It therefore seems likely that many of these elements could be determined polarographically in titanium-, zirconium-, niobium-, tantalum- and tungsten-base materials, since none of the polarograms produced with these latter elements, showed any sign of a wave before −1.0 V.

TABLE 1

Element	Base electrolyte				
	0.1 *M* HF–0.1 *M* NH_4F		0.1 *M* $NaClO_4$		0.1 *M* $HClO_4$
	$E_{\frac{1}{4}}$, V	$E_{\frac{1}{4}}-E_{\frac{1}{4}}$, mV	$E_{\frac{1}{4}}$, V	$E_{\frac{1}{4}}-E_{\frac{1}{4}}$, mV	$E_{\frac{1}{4}}$, V
Silver	Reduced chemically by Hg	—	—	—	> +0.4
Arsenic (V)	(1) > 0 (V → III)	—	—	—	—
	(2) Small very irreversible wave centred on-0.8 V (III → 0?)	—	—	—	—
Antimony (V)	(1) Reduced chemically by Hg to Sb^{III}	—	—	—	—
	(2) −0.65 (III → 0)	90 (19)	—	—	—
Copper (II)	Overlapping double wave +0.08; −0.07	Waves cover 0.3 V	+0.012[c]	60 (28)	—
Bismuth	−0.131	19 (19)	—	21 (19)	+0.028
Tin (II)	(1) −0.228*	−33 (−28)	—	−29 (−28)*	+0.053
	(2) −0.602	27 (28)	—	30 (28)	−0.392
Lead	−0.402	28 (28)	−0.375	32 (28)	—
Thallium (I)	−0.455	54 (56)	−0.447	55 (56)	—
Uranium (VI)	−0.51	270 (?)	—	—	—
Iron (III)	(1) −0.52 (III → II)	140 (56)	—	—	> 0 (III→ II)
	(2) No redn. before H^+ wave (II → 0)				No redn. be-fore H^+ wave (II → 0)
Molybdenum (VI)	(1) −0.53 (VI → V)	130 (56)	—	—	—
	(2) Incomplete sepn. from H^+ wave (V → III)	—	—	—	—
Cadmium	−0.585	30 (28)	−0.578	29 (28)	—
Antimony (III)	−0.62[a]	100 (19)	—	40 (19)	−0.174
Arsenic (III)	Overlapping double wave −0.84; −0.88[b]	Waves cover 0.6 V	—	—	—
Nickel	−0.999	61	−0.983	64	—
Zinc	−1.114	35 (28)	−0.997	31 (28)	—
Chromium (III)	Incomplete sepn. from H^+ wave	—	—	57 (56)	−0.77; −1.05[e] Mixture of complexes?
Indium	Incomplete sepn. from H^+ wave	—	—	120 (19)	−0.96[f]

Element	Base electrolyte				
	0.1 *M* HF–0.1 *M* NH_4F		0.1 *M* $NaClO_4$		0.1 *M* $HClO_4$
	E_i, V	E_i–E_l, mV	E_i, V	E_i–E_l, mV	E_i, V
Cobalt	Incomplete sepn. from H^+ wave	—	−1.187	62	—
Vanadium (IV)	Incomplete sepn. from H^+ wave	—	—	—	—
Rhenium (VII)	Incomplete sepn. from H^+ wave	—	—	—	—
Titanium (IV)	Incomplete sepn. from H^+ wave	—	—	—	—
Tungsten (VI)	Incomplete sepn. from H^+ wave	—	—	—	—
Iron (II)	No redn. before H^+ wave	—	−1.283[d]	52	—
Manganese (II)	No redn. before H^+ wave	—	−1.457[e]	30 (28)	—
Gallium	No redn. before H^+ wave	—	—	—	Incomplete sepn. from H^+ wave
Tin (IV)	No redn. before H^+ wave	—	—	—	No redn. before †H^+ wave
Niobium (V)	No redn. before H^+ wave	—	—	—	—

* An anodic wave ($Sn^{II} \rightarrow Sn^{IV}$).

† The base electrolyte here was 2 *M* perchloric acid.

[a] [b] [c] [d] [e] These solutions were 0.0001% (w/v), 0.0004% (w/v), 0.001% (w/v), 0.002% (w/v) and 0.004% (w/v) in Triton X-100 respectively.

[f] This solution was 0.002% (w/v) in gelatine.

The concentration of each species in the base electrolyte was 2×10^{-4} *M* except for the following, lead—a saturated solution, titanium (IV) 10^{-3} *M*, niobium (V) 3×10^{-4} *M*, molybdenum 6×10^{-4} *M*, and tungsten (VI) 10^{-3} *M*.

For the 2×10^{-4} *M* solutions of metallic ions in 0.1 *M* HF–0.1 *M* NH_4F the diffusion currents lay between 1.5 and 3.0 μA except for iron (III), which produced a smaller wave, and for arsenic (III) and antimony (III), which gave much larger waves. These waves were obtained with t in the range 4.5 to 5.5 sec and m in the range 1.94–2.80 mg sec^{-1}.

The figures shown in parentheses are the values of E_i–E_l expected for reversible waves.

However, the recorded polarograms had been obtained on solutions $\leqslant 10^{-3}$ *M* in the metal, and it was expected that the very irreversible reduction waves for titanium (IV), niobium (V) and tungsten (VI) would start earlier if the metals were present at higher concentrations. In order to verify this, polarograms were obtained for 10^{-1} *M* solutions of titanium (IV), zirconium, niobium (V), tantalum and tungsten (VI) in

1 *M* hydrofluoric acid–1 *M* ammonium fluoride using a sensitivity setting on the Sargent Polarograph such that a full scale deflection corresponded to a current of 5 μA. Since 2×10^{-4} *M* solutions of tin, lead, etc. (see above), produced diffusion currents of 1.5–3 μA at the same sensitivity setting, the use of 10^{-1} *M* solutions of the base materials should make possible the determination of tin, lead, etc., in these base materials when present in amounts greater than 0.01%. Table 2 contains information on the polarograms obtained with these 10^{-1} *M* solutions and lists the common elements that may be determined in these base materials.

TABLE 2

Element	Applied potential at start of irreversible wave (V)	Common elements that may be determined
Titanium (IV)	−0.8	Cu, Bi, Sn, Pb, Tl, Cd
Zirconium	−1.2 (H^+ wave)	Cu, Bi, Sn, Pb, Tl, Cd, Mo, Sb, Fe, Ni, Zn
Niobium (V)	−0.9	Cu, Bi, Sn, Pb, Tl, Cd, Mo, Sb
Tantalum	−0.9	
Tungsten (VI)	−0.5	Cu, Bi, Sn, Pb

A comparison of the half-wave potentials in Table 1 for the reversible waves obtained with fluoride and perchlorate media, verifies that cadmium, lead and thallium (I) form only weak complexes with fluoride ions, while bismuth and tin (II) are complexed to a moderate extent. Unfortunately, the elements, which form strong fluoride complexes,[8] produce very irreversible polarographic waves. For this reason, only molybdenum (VI) among titanium (IV), zirconium, niobium (V), tantalum, molybdenum (VI) and tungsten (VI), gave in hydrofluoric acid–ammonium fluoride a polarographic reduction wave that could be used for analysis. However, this wave was very irreversible and it was decided to reduce the concentration of free fluoride ion associated with the molybdenum by using base electrolytes consisting of hydrofluoric acid with hydrochloric or sulphuric acid, with a view to obtaining more reversible molybdenum waves, and possibly reduction waves for titanium, niobium and tungsten, that might be analytically useful.

Table 3 shows half-wave potential data obtained for molybednum in hydrochloric acid–hydrofluoric acid and sulphuric acid–hydrofluoric acid media.

TABLE 3

Half-wave potential data for molybdenum

Base electrolyte	Reduction of Mo (VI)→Mo (V)		Reduction of Mo (V)→Mo (III)	
	$E_{\frac{1}{4}}$, V	$E_{\frac{1}{4}}-E_{\frac{1}{2}}$, mV	$E_{\frac{1}{4}}$, V	$E_{\frac{1}{4}}-E_{\frac{1}{2}}$, mV
0.5 *M* NH_3–0.5 *M* NH_4F	No reduction	—	No reduction	—
0.5 *M* HF–0.5 *M* NH_4F	−0.53	130	−1.22*	120
2 *M* HCl	Wave coming immediately after oxidation of Hg	—	−0.07	40
2 *M* HCl–0.5 *M* HF	Wave coming immediately after oxidation of Hg	—	−0.18	60
6 *M* HCl–0.5 *M* HF	Wave coming immediately after oxidation of Hg	—	Wave coming immediately after oxidation of Hg	—
1 *M* H_2SO_4	>0	—	−0.25	190
0.1 *M* H_2SO_4–0.5 *M* HF	−0.13	120	−0.67	140
0.5 *M* H_2SO_4–0.5 *M* HF	−0.06	100	−0.52	140
1.0 *M* H_2SO_4–0.5 *M* HF	−0.02	80	−0.40	110
2.0 *M* H_2SO_4–0.5 *M* HF	−0.01	100	−0.33	80
4.0 *M* H_2SO_4–0.5 *M* HF	>0	—	−0.25	80
6.0 *M* H_2SO_4–0.5 *M* HF	Wave distorted. The H_2SO_4 attacks the agar bridge			

* Upper end coalesces with the wave for the reduction of hydrogen ion.

All solutions were 10^{-3} *M* in molybdenum.

The $E_{\frac{1}{4}}-E_{\frac{1}{2}}$ values are expressed in mV. The $E_{\frac{1}{4}}-E_{\frac{1}{2}}$ values expected for reversible waves are 56 mV for Mo (VI) → Mo (V) and 28 mV for Mo (V) → Mo (III).

Sulphuric acid–hydrofluoric acid solutions are obviously more suitable base electrolytes than hydrochloric acid–hydrofluoric acid solutions. With the sulphuric acid–hydrofluoric acid base electrolytes, it will be noticed that the higher the ratio of the concentrations of sulphuric acid: hydrofluoric acid, the more positive are the half-wave potentials for both reduction waves. While the first reduction wave obtained in 0.5 *M* hydrofluoric acid–0.5 *M* ammonium fluoride could be used for quantitative determinations, the first reduction wave in 0.5 *M* sulphuric acid–0.5 *M* hydrofluoric acid was preferred for this purpose, because it is more reversible than the former wave. If a mercury pool anode is used, a sufficient length of the residual current line is obtained for accurate measurements of diffusion current to be made on this wave.

It was expected that 10^{-3} *M* solutions of titanium (IV), niobium (V) and tungsten (VI) in 0.5 *M* sulphuric acid–0.5 *M* hydrofluoric acid

would display irreversible waves at potentials more negative than −0.5 V, and actual information for such solutions is shown in Table 4.

TABLE 4

Element	Applied potential at start of irreversible wave (V)	
	10^{-3} *M* solutions	5×10^{-2} *M* solutions
Tungsten (VI)	−0.6	−0.1
Titanium (IV)	−0.7	0
Niobium (V)	−1.0	−0.8

These irreversible waves were obtained at a sensitivity setting on the Sargent polarograph such that a full-scale deflection corresponded to 20 μA. This sensitivity setting was the one generally employed for $10^{-3}M$ solutions of molybdenum (VI). Table 4 also contains details about these elements when present at concentrations of 5×10^{-2} *M* using the same sensitivity setting on the polarograph. The start of reduction waves for zirconium and tantalum will be more negative than −0.8 *V*.

It is therefore obvious that low concentrations of molybdenum (VI) could be determined polarographically in the presence of at least 50-fold excesses of zirconium, niobium and tantalum if i_d/C for molybdenum is a constant. Molybdenum could also be determined in the presence of titanium and tungsten provided that the ratio of the concentrations of titanium or tungsten : molybdenum was not much greater than unity.

On the basis of the information described in this paper, work is now being undertaken to develop polarographic methods for the determination of copper, tin, lead, molybdenum, nickel, etc., in alloys containing titanium, zirconium, niobium, tantalum and tungsten.

We also intend to investigate the possibility of determining polarographically major amounts of tin and lead in non-ferrous alloys using fluoride base electrolytes. From Table 1 it can be seen that the oxidation wave for tin (II) and the reduction waves for tin (II) and lead are well separated. Very few base electrolytes are known in which a direct polarographic determination of both tin and lead can be made.[9]

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8

SHORT PAPERS

The Polarographic Determination of Molybdenum in Niobium-base Alloys

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In a recent paper[1] it was stated that molybdenum^{VI} produces in 0·5 M hydrofluoric acid - 0·5 M sulphuric acid mixture two waves that can be used for analysis. The first wave results from the reduction of molybdenum^{VI} to molybdenum^{V}, $E_{\frac{1}{2}} = -0{\cdot}06$ volt with respect to the saturated calomel electrode ($E_{\frac{1}{4}} - E_{\frac{1}{2}} = 100$ mV), and the second wave from the reduction of molybdenum^{VI} to molybdenum^{III}, $E_{\frac{1}{2}} = -0{\cdot}52$ volt ($E_{\frac{1}{4}} - E_{\frac{1}{2}} = 140$ mV). With this supporting electrolyte, titanium, zirconium, niobium, tantalum and tungsten are held in true solution. For a 10^{-3} M solution of molybdenum^{VI}, 50-fold excesses of zirconium, niobium^{V} and tantalum, and 5-fold excesses of titanium^{IV} and tungsten^{VI} have no interfering effects on the first molybdenum wave.

A method based on these polarographic results has now been applied to the determination of molybdenum in niobium-base alloys.

Method

Apparatus—

Polarograph—A Sargent model XV polarograph was used.

Dropping mercury electrode—This was constructed from Teflon according to the method of Raaen.[2] Polarograms were recorded by using a Teflon segment with an orifice of 60 μ. This segment was fitted to a suitable length of Sargent "2 to 5"-second glass capillary.

Polarographic cell—A 20-ml polythene specimen tube was modified for this purpose. This consisted of sealing a platinum wire into the side of the tube 3 mm from the base to make electrical contact to a mercury-pool anode. A lead-in tube for oxygen-free nitrogen was also sealed into the side of the tube near the base. The lid of the specimen tube was adapted to take a lead-in tube for nitrogen to pass over the surface of the solution in the cell. A hole of suitable diameter was cut from the lid for the dropping mercury electrode. The cell was immersed in a tank thermostatically controlled at 25·0° C.

Reagents—

Hydrofluoric, nitric and sulphuric acids—These were of analytical reagent grade.

Standard molybdenum^{VI} solution—A suitable weight of Specpure molybdenum trioxide, obtained from Johnson, Matthey & Co. Ltd., was dissolved in boiling ammonia solution sp.gr. 0·88, in a polytetrafluoroethylene beaker, the solution was evaporated to dryness, and the residue dissolved in 0·5 M hydrofluoric acid - 0·5 M sulphuric acid. This stock solution contained 0·402 mg of molybdenum trioxide per g of solution. Less concentrated solutions of molybdenum^{VI} in this acid mixture were made by dilution. All solutions containing hydrofluoric acid were stored in polythene bottles.

The constancy of the ratio of diffusion current to concentration—

Six standard molybdenum^{VI} solutions in the concentration range of 0·028 to 0·118 mg per g (approximately 2×10^{-4} to 8×10^{-4} molal) were prepared in 0·5 M hydrofluoric acid - 0·5 M sulphuric acid mixture and polarograms were recorded over the range of applied potential of 0 to −1 volt. The anode was a still mercury pool. The wave heights were measured in each instance from the residual-current line to the plateau of the first molybdenum wave at a potential 0·15 volt more negative than the half-wave potential. This procedure was adopted, since, unlike the saturated calomel electrode, the potential of the mercury pool anode was not constant, but, in our work, varied within the range of +0·27 to +0·34 volt *versus* the standard calomel electrode. In all instances the sensitivity setting on the polarograph was 0·02 μA per mm, and by using this conversion factor, wave heights were expressed as diffusion currents in microamps. Maximum current readings rather than average current readings were taken, as recommended in the instrument manual.

A plot of diffusion current *versus* molybdenum concentration produced a straight-line graph that passed through the origin, thus proving that the diffusion current is directly proportional to concentration, as expected. For all polarograms, the head of mercury was 44·5 cm and a 60-μ Teflon segment was used. Under these conditions, m (the flow-rate of mercury) was 1·563 mg per second and t (the drop time) was 4·80 seconds at an applied potential of −0·21 volt with respect to the standard calomel electrode.

The diffusion current constant, $I = i_d/(c\,m^{2/3}t^{1/6})$, calculated from the slope of the graph and the values of m and t, was 2·01, i_d being the maximum and not the average current. The concentration, c, is expressed in millimoles per 1000 g.

In order to assess the precision of a polarographic determination of molybdenum^{VI} in 0·5 M hydrofluoric acid - 0·5 M sulphuric acid mixture, diffusion currents were calculated for each solution from the slope of the graph and compared with the measured diffusion currents as shown in Table I.

TABLE I

STATISTICAL RESULTS FOR THE POLAROGRAPHIC DETERMINATION OF MOLYBDENUM

Solution number	Concentration of molybdenum trioxide, mg per g	i_d calculated, μA	i_d measured, μA	Error, μA
1	0·028	0·68	0·68	0·00
2	0·045	1·09	1·11	+0·02
3	0·065	1·58	1·56	−0·02
4	0·082	1·99	1·97	−0·02
5	0·100	2·43	2·43	0·00
6	0·118	2·88	2·91	+0·03

A mean error of almost zero verifies that the straight line through the origin is, in fact, the best straight line through the six points. The standard deviation from zero for the error is $0{\cdot}02_0$ μA. For an $8{\cdot}2 \times 10^{-4}$ molal solution of molybdenum (number 6), this amounts to a relative standard deviation of 0·7 per cent.

DETERMINATION OF MOLYBDENUM IN ALLOYS—

Dissolve a weighed portion of alloy containing about 5 mg of molybdenum in 4 ml of nitric acid, sp.gr. 1·42, in a platinum crucible. Add 1·39 ml of sulphuric acid, sp.gr. 1·84, from a burette and heat the solution to fumes of sulphur trioxide. Cool the crucible, add 1·11 ml of concentrated hydrofluoric acid dropwise from a polythene burette, cool the solution and transfer it to a previously weighed polythene bottle. Dilute the solution to 50 ml with water, and re-weigh the bottle. Calculate the concentration of alloy in the solution in milligrams per gram.

Place approximately 10 ml of solution in the polarographic cell and de-oxygenate by bubbling oxygen-free nitrogen through it for 15 minutes. Add sufficient mercury to cover the platinum wire and record a polarogram from 0 to −1·0 volt with a sensitivity setting on the instrument such that the full length of the current axis corresponds to 5 μA, *i.e.*, 0·02 μA per mm on the Sargent model XV polarograph.

Measure the diffusion current for the first molybdenum wave at an applied potential 0·15 volt more negative than the half-wave potential and read the concentration of molybdenum in the solution from a calibration graph prepared with standard solutions of molybdenum examined polarographically under the same conditions as used for the alloy. Hence calculate the concentration of molybdenum in the alloy. (For alloys, we used the calibration graph prepared to verify that i_d/c is a constant.)

RESULTS

The polarographic method was applied to the determination of molybdenum in three niobium-base alloys that also contained tungsten. The results are given in Table II and are compared with those obtained by a thiocyanate spectrophotometric method.[3,4]

The polarographic result for each sample was obtained from a diffusion current that was the average of two measurements taken from two polarograms of the same solution. The spectrophotometric result for each sample was calculated from an optical-density value that was the average of two optical-density readings for two different aliquots of the same sample solution.

These results are considered to be satisfactory, since the relative standard deviation of each method is about 1 per cent. The polarographic method is straightforward and rapid, and could also be used for determining molybdenum in zirconium- and tantalum-based alloys.

TABLE II

DETERMINATION OF MOLYBDENUM IN ALLOYS

Alloy	Approximate composition	Sample number	Molybdenum found— polarographically	Molybdenum found— spectrophotometrically
A	Niobium base, 15 per cent. tungsten, 5 per cent. molybdenum	1	4·90	4·95
		2	4·90	5·00
B	Niobium base, 15 per cent. tungsten, 5 per cent. molybdenum	1	5·10	5·10
		2	5·10	5·10
C	Niobium base, 15 per cent. tungsten, 5 per cent. molybdenum, 1 per cent. zirconium	1	4·65	4·65
		2	4·75	4·65

No interference is to be expected from elements whose half-wave potentials in acidic solution are more negative than −0·5 volt *versus* the standard calomel electrode, which category includes chromium, magnanese, cobalt and nickel. $Iron^{III}$, if present in more than trace amounts, interferes with the molybdenum determination, since, in 0·5 M hydrofluoric acid - 0·5 M sulphuric acid mixture, the plateau of an irreversible iron wave ($iron^{III} \rightarrow iron^{II}$) is not reached until the potential is −0·2 volt *versus* the standard calomel electrode.

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Polarography in neutral fluoride solution with particular reference to lead

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TRACE amounts of lead have a detrimental effect on the creep-resisting properties of nickel-base[1] and other high-temperature alloys and it is desirable to know the lead content of such alloys. Lead can be determined spectrophotometrically in many of these alloys after a solvent extraction separation, but a fast, direct method for lead would be attractive. This paper outlines a direct polarographic method, which should be suitable for the determination of trace amounts of lead in high-temperature alloys of low iron content.

EXPERIMENTAL

Apparatus

Polarograph. A Sargent model XV polarograph was used. The micro-range extender for this instrument was occasionally employed.

Dropping mercury electrode. This was constructed from a 15-cm length of "Veridia" Pyrex glass capillary tubing of 60-μ bore obtained from Chance Brothers Limited, Birmingham, England.

Polarograph cell. This was a Meites-type H-cell with a saturated calomel electrode in the electrode compartment and an agar-saturated potassium chloride bridge. Fifty ml of solution were used in the solution compartment. The cell was immersed in a tank thermostatically controlled at 25·0°. Oxygen-free nitrogen was used to free the solution from dissolved oxygen.

Reagents

Hydrofluoric and nitric acids, ammonium fluoride and aqueous ammonia were of analytical-reagent grade.

Standard lead solution. This was exactly $10^{-3}M$, prepared from the appropriate weight of analytical-reagent grade lead nitrate crystals, of which the lead content had been previously determined by complexometric titration with standard EDTA solution. The lead solutions used in obtaining the calibration graphs were prepared from this standard lead nitrate solution by dilution with $5M$ neutral ammonium fluoride solution and water.

RESULTS AND DISCUSSION

Previous polarographic investigations for 28 metallic ions in $0{\cdot}1M$ hydrofluoric acid–$0{\cdot}1M$ ammonium fluoride[2] had shown that lead ions produced a reversible reduction wave at −0·402 V *vs.* the saturated calomel electrode. Metallic species, which were reduced in the vicinity of the lead and which would, therefore, interfere with a lead determination, were thallium(I) $E_{\frac{1}{2}} = -0{\cdot}455$ V, uranium(VI) $E_{\frac{1}{2}} = -0{\cdot}51$ V, iron(III) $E_{\frac{1}{2}} = -0{\cdot}52$ V and molybdenum(VI) $E_{\frac{1}{2}} = -0{\cdot}53$ V. Because ions of metals in the +3 and higher oxidation states are complexed strongly by fluoride, while most singly- and doubly-charged ions are only slightly complexed,[3] it was decided to investigate the polarographic properties of metallic ions in a more strongly complexing solution, namely $1M$ ammonium fluoride at pH 7; it was expected that in such a base electrolyte the half-wave potential for the reduction of iron(III)—iron being a common constituent of high-temperature alloys—would be moved to a considerably more negative potential, while the half-wave potential for lead would be only slightly more negative than before. The half-wave potentials for molybdenum(VI) and uranium(VI) in $1M$ ammonium fluoride at pH 7 were also expected to be considerably more negative than the values quoted above because of the increase in pH from 3·2 for $0{\cdot}1M$ hydrofluoric acid–$0{\cdot}1M$ ammonium fluoride, to 7·0.

In practice, these hopes were realised and polarographic data for 35 ions in $1M$ ammonium fluoride at pH 7 are given in Table I. Another advantage of $1M$ ammonium fluoride at pH 7 as base electrolyte is that polarograms can be recorded using a dropping mercury electrode (D.M.E.) constructed from a Pyrex glass capillary, which is not attacked by fluoride ions at pH 7. With $0{\cdot}1M$ hydrofluoric acid–$0{\cdot}1M$ ammonium fluoride, glass capillaries are attacked immediately and

satisfactory polarograms cannot be produced with them. The data previously reported for 0·1*M* hydrofluoric acid–0·1*M* ammonium fluoride were obtained with a Teflon dropping mercury electrode constructed according to the method of Raaen.[4] Although such a D.M.E. is perfectly satisfactory for acidic fluoride solutions, its construction demands considerable manipulative skill and most analytical chemists would prefer to buy glass capillaries rather than construct their own Teflon capillary.

TABLE I

Element	$E_{\frac{1}{4}}$, V	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$, *m*V
Silver	>0	—
Copper(II)	Overlapping double wave, about +0.02; −0.16	Waves cover 0·35 V; incomplete separation of first wave from mercury wave.
Iron(II)	(1) about −0·06†	Incomplete separation from mercury wave
	(2) −1·44	63
Vanadium(V)	(1) About −0·12; small wave with maximum.*	Wave covers range −0·06 to −0·60 V.
	(2) −0·79; small wave	140
	(3) −1·40	100
Bismuth	−0.265	35(19)
Tin(II)	(1) −0·412†	−34(−28)
	(2) −0·703	29(28)
Lead	−0·453	30(28)
Thallium(I)	−0·463	54(56)
Tellurium(IV)	−0·52	140
Cadmium	−0·614	27(28)
Antimony(III)	−0·74	95(19)
Iron(III)	(1) −0.77(III → II)	160(56)
	(2) −1·47(II → 0)	100
Uranium(VI)	Overlapping double wave, −0·80; −1·11	Waves cover range −0.5 to −1·4 V.
Nickel	−1·05	71
Zinc	−1·148	54(28)
Tellurium(VI)	−1·24	85
Selenium(IV)	−1·28	100
Cobalt(II)	−1·32	110
Titanium	−1·37	95(56)
Arsenic(III)	About −1·40; maximum present.*	Wave covers range −1·1 V to final rise at −1.8 V.
Rhenium(VII)	About −1·44; Maximum present.*	Wave covers range −1·2 V to final rise
Vanadium(IV)	Overlapping double wave, −1·45; about −1·68	Waves cover range −1·2 V to final rise
Gallium	−1·50	About 120(19)
Manganese(II)	−1·55	About 40(28)

† Oxidation wave.

* This maximum was not completely suppressed with the maximum permissible concentration of Triton X-100 or gelatine, namely 0·004% w/v and 0·1% w/v, respectively.

The reduction waves for antimony(V), chromium(III), niobium(V), tin(IV) and tungsten(VI) started just before the ammonium ion wave. There were no reduction waves for arsenic(V), indium, molybdenum(VI), selenium(VI), tantalum(V) and zirconium.

The concentration of all ions was $2 \times 10^{-4}M$ except for bismuth where a saturated solution ($<2 \times 10^{-4}M$) was used.

The figures shown in parenthesis are the $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ values expected for reversible reductions.

In 1*M* ammonium fluoride at pH 7, reduction waves for vanadium(V), thallium(I), tellurium(IV) and uranium(VI) interfere with the lead wave as does the oxidation wave for tin(II). Equal molar amounts of copper, bismuth, cadmium, antimony(III) and iron(III) have no interfering effect on the lead wave, but appreciably larger amounts of copper and bismuth will cause difficulty in the determination of lead using a d.c. polarograph. Interference from cadmium, antimony(III) and iron(III) occurs when the molar ratios of these elements to lead exceed 10:1, 4:1 and 4:1, respectively. There is no interference from the other 24 ions.

Thallium and uranium are unlikely to be present in high-temperature alloys and it may be possible to arrange for vanadium, tellurium and tin to be in the +4, +6 and +4 oxidation states, respectively, where they no longer interfere.

In 1*M* ammonium fluoride at pH 7, the diffusion current was found to be directly proportional to lead concentration, as expected, in the ranges 10^{-5} to $10^{-4}M$ and 10^{-6} to $10^{-5}M$. In the range 10^{-5} to $10^{-4}M$, the standard deviation of the error in diffusion current was 0·0059 μA, which corresponds to a relative standard deviation of 0·9% at a lead concentration of $10^{-4}M$. In the range 10^{-6} to $10^{-5}M$, where the micro-range extender was employed, the standard deviation of the error in diffusion current was 0·0014 μA, corresponding to a relative standard deviation of 2·0% at a lead concentration of $10^{-5}M$. The error in diffusion current is expressed by i_d(measured) — i_d(calculated), where the values of i_d(calculated) are points exactly on the straight-line calibration graph of diffusion current *vs.* concentration.

Lead in high-temperature alloys often occurs in amounts less than 50 ppm and the authors' instrument was not sufficiently sensitive to determine such small amounts of lead. One nickel–titanium addition alloy containing 92 ppm of lead, was, however, analysed by the method described below, where the micro-range extender was employed on the Sargent recording polarograph. A lead content of 86 ppm with a standard deviation of 11 ppm was obtained. This corresponds to polarographing a lead solution of concentration $1{\cdot}65 \times 10^{-6}M$. A much more precise result would have been obtained with a more sensitive polarograph.

The lead content of the alloy (92 ppm) had been originally determined by solvent extraction of the lead from an ammoniacal cyanide–tartrate solution at pH 9·5 with a solution of dithizone in carbon tetrachloride, followed by spectrophotometric measurement of the lead dithizonate complex.

Method for analysis of the nickel-titanium alloy

Dissolve 0·2 g of alloy in 5 ml of concentrated hydrofluoric acid plus 1 ml of concentrated nitric acid. Evaporate the solution just to dryness and dissolve the residue in 5 ml of concentrated hydrofluoric acid. Re-evaporate the solution just to dryness. Dissolve the residue in 25 ml of 2*M* hydrofluoric acid and add concentrated ammonia solution until the pH is 7·0 when determined with a pH meter. Dilute the solution to 50 ml in a graduated flask. Record a polarogram for this solution over the range of 0 to −1·0 V against the saturated calomel electrode and measure the diffusion current of the lead wave in microamps. Determine the concentration of lead in the solution from a suitable calibration graph and hence calculate the amount of lead in the alloy.

CONCLUSION

The authors are of the opinion that this work performed with a d.c. polarograph indicates that direct polarography in 1*M* ammonium fluoride adjusted to pH 7, in association with a differential cathode ray or pulse polarograph, could be employed for the precise determination of lead in high-temperature alloys in amounts greater than 1 ppm. Parts per million of trace metals in alloys have already been determined using a square wave polarograph.[5] With such instruments it is reasonable to expect that a much greater iron(III):lead ratio could be tolerated.

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Summary—The polarographic behaviour of 35 ions in 1*M* ammonium fluoride solution adjusted to pH 7 has been investigated. In this base electrolyte lead is reduced reversibly and, except for considerably larger amounts of copper, bismuth, cadmium, antimony(III) and iron(III), the only ions interfering with the d.c. polarographic determination of lead are vanadium(V), thallium(I), tellurium(IV), uranium(VI) and tin(II). By arranging for vanadium, tellurium and tin to be in the +4, +6 and +4 oxidation states, respectively, interference from these elements could be eliminated and a selective polarographic method for lead is available.

Résumé—On a étudié le comportement polarographique de 35 ions en solution dans le fluorure d'ammonium 1 *M* ajusté à pH 7. Dans cet électrolyte de base le plomb est réduit réversiblement et, sauf lorsqu'il y a des quantités considérablement plus élevées de cuivre, bismuth, cadmium, antimoine(III) et fer(III), les seuls ions qui interfèrent dans le dosage du plomb par polarographie en courant continu sont le vanadium(V), le thallium(I), le tellurium(IV), l'uranium(VI) et l'étain(II). En amenant le vanadium, le tellurium et l'étain aux degrés d'oxydation +4, +6 et +4 respectivement, on peut éliminer l'interférence de ces éléments et disposer d'une méthode polarographique sélective du plomb.

Zusammenfassung—Das polarographische Verhalten von 35 Ionen in 1 M Ammonfluoridlösung bei pH 7 wurde untersucht. In diesem Trägerelektrolyten wird Blei reversibel reduziert. Außer beträchtlich größeren Mengen Kupfer, Wismut, Cadmium, Antimon(III) und Eisen(III) stören die gleichstrompolarographische Bestimmung von Blei nur Vanadin(V), Thallium(I), Tellur(IV), Uran(VI) und Zinn(II). Bringt man Vanadin, Tellur und Zinn auf die Oxydationsstufen +4, +6 und +4, ist die Störung durch diese Elemente beseitigt und Blei kann selektiv polarographisch bestimmt werden.

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10

The Polarographic Determination of Lead after Cation-exchange Separation

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From M hydrofluoric acid solution, lead, cobalt, copper(II), manganese(II), nickel and a small part of chromium(III) are strongly adsorbed on a column of strongly acidic cation-exchange resin in the hydrogen form, while other elements present in steel are either not adsorbed or only weakly adsorbed, and are removed from the column on washing it with M hydrofluoric acid.

On elution with 2 M hydrochloric acid, the lead is removed from the column and determined by d.c. polarography. This method is applied to the determination of lead (>0·01 per cent.) in steels.

THE direct polarographic determination of lead in the presence of aluminium, chromium(III), cobalt, copper, iron(II), manganese, nickel, tin(IV) and zinc is straightforward, and alloys containing these elements have been satisfactorily analysed for lead.[1,2,3] However, the polarographic determination of lead is more difficult in the presence of titanium(IV) and molybdenum(VI), elements often present in high-alloy steels, because these species often produce reduction waves that interfere with the lead wave.

Hamza and Headridge,[4] using M ammonium fluoride adjusted to pH 7 as the base electrolyte, obtained a reversible reduction wave for lead, $E_{\frac{1}{2}} = -0{\cdot}453$ volt against a S.C.E., with which there is no interference from molybdenum(VI), titanium(IV) and vanadium(IV). However, if that base electrolyte was used for the direct determination of lead in steel, there would be interference from iron(III), which produces an irreversible reduction wave, $E_{\frac{1}{2}} = -0{\cdot}77$ volt against a S.C.E., that interferes with the lead wave when the molar ratio of iron(III) to lead exceeds 4 to 1. Although attempts were made to remove interference from iron(III) by reducing it quantitatively to iron(II), these were unsuccessful because iron(II) is a powerful reducing agent in M ammonium fluoride.

It was, therefore, decided to examine the possibility of separating lead from iron(III), molybdenum(VI), titanium(IV) and vanadium(V) using a cation-exchange resin.

Headridge and Dixon[5] have reported that aluminium, iron(III) and vanadium(V) are scarcely adsorbed on the cation-exchange resin, ZeoKarb 225, in the hydrogen form, from M hydrofluoric acid. On the other hand, cobalt, copper (II), nickel and manganese(II) are strongly adsorbed. The behaviour of chromium(III) was unusual. From boiled solutions, the chromium(III) was obviously present in two complexes not in rapid equilibrium. The complex present in major amount was not adsorbed by the cation-exchange resin from M hydrofluoric acid, but the minor complex, possibly $Cr(H_2O)_4F_2^+$, was strongly adsorbed.

Nikitin[6] has reported that lead is adsorbed by a cation-exchange resin from M hydrofluoric acid. This is to be expected since lead, like copper(II), complexes only weakly with fluoride,[7] and copper(II) is strongly adsorbed by ZeoKarb 225 from M hydrofluoric acid. arsenic(III) and (V), antimony(III) and (V), tin(IV), titanium(IV), zirconium, niobium(V), tantalum, molybdenum(VI) and tungsten(VI) are either not adsorbed or only weakly adsorbed by a cation-exchange resin from M hydrofluoric acid.[6,8,9]

A simple method is therefore available for separating lead from elements that interfere with its polarographic determination. The alloy is dissolved in a mixture of hydrofluoric and nitric acids, the excess of nitric acid is removed by evaporation, and a M hydrofluoric acid solution of the metallic ions is passed down a column of ZeoKarb 225 in the hydrogen form. Lead, cobalt, copper(II), manganese(II), nickel and a small fraction of the chromium(III) are adsorbed. On washing with 16 column volumes of M hydrofluoric acid, arsenic(V), antimony(V), aluminium, iron(III), tin(IV), titanium(IV), zirconium, vanadium(V), niobium(V), tantalum, molybdenum(VI), tungsten(VI) and most of the chromium(III) are removed from the column.

Hydrochloric acid (2 M) was considered to be a suitable eluant for lead. Most, or all, of the copper(II), cobalt, chromium(III), manganese(II) and nickel accompany the lead, but cobalt, manganese and nickel do not interfere with the polarographic determination of lead in a base electrolyte of M hydrochloric acid. Copper in amounts considerably in excess of the lead causes difficulties with the d.c. polarographic determination of lead in M hydrochloric

acid, but not with a differential cathode-ray or pulse polarographic determination. Chromium(II) interferes with the polarographic determination of lead in M hydrochloric acid, and, if more than a trace of chromium(III) is present, a base electrolyte of 0·5 M acetic acid - 0·5 M sodium acetate - 0·5 M sodium chloride may be used. There is no interference from chromium(III) in this base electrolyte.

A polarographic method based on this scheme is now described for the determination of lead in steels.

Experimental

Apparatus—

Polarograph—A Sargent model XV polarograph was used.

Polarographic cell—This was a Meites-type H-cell with a saturated calomel electrode in the electrode compartment and an agar-saturated potassium chloride bridge. The volume of solution used in the solution compartment was 40 ml. The cell was immersed in a water tank thermostatically controlled at 25·0° C. Oxygen-free nitrogen was used to free the solution from dissolved oxygen.

Polythene column—This was constructed as follows. The bottom of part of a polythene specimen tube, of length 2·0 cm and internal diameter 1·3 cm, was drilled with eight holes of diameter 0·05 cm, and half-filled with polythene drillings. A polythene disc, of diameter 1·35 cm, was also drilled with eight holes of diameter 0·05 cm, and was forced into the specimen tube until it came into contact with the drillings. A piece of polythene tubing, 34 cm long with an internal diameter of 1·0 cm and external diameter of 1·3 cm, was then inserted into, and welded to, the specimen tube. A short piece of flexible plastic tubing was pushed over the lower end of the specimen tube and fitted with a screw clamp.

An aqueous slurry of ZeoKarb 225 (SRC14), of mesh size 52 to 100, was added to the column to produce a resin bed 3·8 cm high and 3·0 ml in volume. The top 30 cm of the column acted as a reservoir. The resin was washed with 5 M hydrochloric acid to convert it entirely to the hydrogen form, and then by water until free from chloride ions. It was then ready for use.

Reagents—

Hydrochloric, hydrofluoric and nitric acids—These were of analytical-reagent grade.

High-purity iron—This was Specpure iron obtained from Johnson, Matthey and Company Limited.

Standard lead solution—Prepare an exactly 10^{-3} M solution from the appropriate weight of analytical-reagent grade lead nitrate crystals, the lead content of which has been previously determined by a complexometric titration with standard EDTA solution. The lead solutions used in obtaining the calibration graph are prepared from this standard lead solution by diluting with 2 M hydrochloric acid and water.

Method—

Dissolve 1 g of steel in 15 ml of 40 per cent. w/w hydrofluoric acid plus 1 ml of nitric acid, sp.gr. 1·42. Evaporate the solution just to dryness and dissolve the residue in 5 ml of 40 per cent. w/w hydrofluoric acid. Re-evaporate just to dryness. Dissolve the residue in 25 ml of 10 M hydrofluoric acid and dilute the solution to 250 ml in a graduated flask. Immediately transfer the solution to a dry polythene bottle.

Add a suitable aliquot of the M hydrofluoric acid solution to the column of ZeoKarb 225 resin at a flow-rate of approximately 2 ml $minute^{-1}$, such that the quantity of lead, copper, cobalt, manganese, nickel and chromium(III) does not exceed 0·8 millimoles (Notes 1 and 2). Then pass 50 ml of M hydrofluoric acid through the column at a flow-rate of approximately 2 ml $minute^{-1}$, followed by 10 ml of water.

Note 1. Only 2 per cent. of the total chromium(III) is retained by the cation-exchange resin. Make allowance for this when calculating the quantity of adsorbable cations.

Note 2. The column of cation-exchange resin has a total capacity of 3·2 millimoles for doubly charged ions. By restricting the total quantity of strongly adsorbed ions to 0·8 millimoles, only the top 25 per cent. of the column will be occupied by these ions. This is considered to be an adequate safety factor to ensure that no lead is removed when 50 ml of M hydrofluoric acid are subsequently passed through the column.

Elute all of the lead from the column with 50 ml of 2 M hydrochloric acid at a flow-rate of 2 ml minute^{-1}, collecting the effluent in a 100-ml graduated flask. Dilute the solution to the mark with water.

Place 40 ml of this solution in the solution compartment of the polarographic cell and record a polarogram over the potential range of 0 to − 1·0 volt against a S.C.E. When more than a trace of chromium(III) is present in the alloy, transfer 50 ml of the M hydrochloric acid solution by pipette into a 100-ml graduated flask, make up to the mark with 2 M sodium acetate solution, and record a polarogram with this solution. Measure the lead diffusion current at −0·55 volt against a S.C.E. and determine the concentration of lead in the solution from a suitable calibration graph. Hence calculate the amount of lead in the alloy. The authors used a lead calibration graph prepared from six solutions in the concentration range of 10^{-5} to 10^{-4} M. The standard deviation of the error in diffusion current was 0·010 μA corresponding to a relative standard deviation of 1·4 per cent. at a lead concentration of 10^{-4} M. The error in diffusion current is expressed by i_d (measured) - i_d (calculated), where the values of i_d (calculated) are points exactly on the straight-line calibration graph of diffusion current *versus* concentration.

Results

Analysis of synthetic solutions—

Four synthetic solutions of iron(III) plus lead in M hydrofluoric acid were prepared and carried through the cation-exchange and polarographic procedures. Each synthetic solution contained 1 g of Specpure iron. The volume of each solution passed through the column was such that the lead concentrations of the solutions being polarographed were in the range of 4×10^{-5} to 10^{-4} M. The recoveries of lead are shown in Table I.

Table I

The recoveries of lead after a cation-exchange separation from iron(III)

Lead taken, mg	1·00	4·11	8·19	20·3
Lead found, mg	1·00	4·08	8·22	20·3

Analysis of steels—

Two steels were analysed by the recommended method using the calibration graph mentioned previously. The results are shown in Table II.

Table II

Results for the determination of lead in steels

Alloy	Lead content, per cent.	Lead found polarographically, per cent.
Mild steel, BCS 329	0·050	0·050, 0·050
Lead steel, BCS 212/1 ..	0·22	0·21, 0·22

Discussion

A cation-exchange separation of lead prior to its polarographic determination is not actually necessary with the two steels analysed above, but the results, in conjunction with those for the synthetic solutions, are proof of the reliability of the separation scheme.

Although the above results are satisfactory, the metallurgist is primarily interested in amounts of lead less than 100 p.p.m. Because the d.c. polarograph is incapable of producing precise results for lead determinations at concentrations below 100 p.p.m. in the alloy by the above method, we were unable to examine the full potentialities of the method. However, we see no reason why the lower limit of determination should not be lowered to 1 p.p.m. by using a more sensitive polarograph such as a differential cathode-ray or pulse polarograph. Parts per million of trace metals in alloys have already been determined using a square-wave polarograph.[1]

The method should be particularly suitable for the determination of lead in alloy steels containing titanium, vanadium, niobium, tantalum, molybdenum and tungsten, all of which are soluble in a mixture of hydrofluoric and nitric acids. The method could also be applied

to the determination of lead in niobium- and tungsten-base alloys, etc. With all alloys precautions must, of course, be taken to ensure that the column is not overloaded with cobalt, copper, nickel and manganese, which are adsorbed with the lead.

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Voltammetry in ammonium fluoride solution with particular reference to manganese

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POLAROGRAPHIC data for 35 ions in 1*M* ammonium fluoride solution adjusted to pH 7 have already been published[1] and it was logical to extend the investigation to redox systems with potentials more positive than the potential of the oxidation of mercury. This has been done by using a rotating platinum electrode in place of a dropping mercury electrode and the voltammetric behaviour of 19 ions in 1*M* ammonium fluoride is now reported. The voltammetric oxidation of manganese(II) to manganese(IV) can be used for the analysis of solutions containing manganese, and results are reported for the rapid determination of manganese in steels and cast iron of low cobalt content by a voltammetric procedure.

EXPERIMENTAL

Apparatus

Polarograph. A Sargent model XV polarograph was used.

Rotating platinum electrode. This was constructed from Teflon rod 16 cm in length and 1 cm in diameter. The rod was drilled along its length to within 6 mm of the lower end, with a 3-mm drill. The remaining 6 mm of rod were drilled centrally with a 0·3-mm drill and a piece of pure platinum wire of length 2 cm and diameter 0·04 cm was forced through the capillary until 3 mm protruded from the end. The Teflon rod was held in a revolving chuck connected to a constant speed motor (615 rpm). The area of platinum surface exposed to the solutions was 0·0389 cm^2. Mercury was added to the central reservoir to cover the platinum wire, and connection was made to the polarograph by inserting a wire into this mercury.

Polarographic cell. This was a polythene H-cell with a saturated calomel electrode in the electrode compartment and an agar-saturated sodium fluoride bridge. Twenty ml of solution were used in the solution compartment. The cell was immersed in a tank thermostatically controlled at 25·0°. Oxygen-free nitrogen was used to free the solution from dissolved oxygen, but this was not really necessary at potentials positive with respect to the S.C.E.

Reagents

Hydrochloric, hydrofluoric and nitric acids, ammonium fluoride and ammonia were of analytical-reagent grade.

Standard manganese solution. This was exactly $10^{-3}M$, prepared from the appropriate weight of analytical-reagent grade manganous sulphate crystals, of which the manganese content had been previously determined by complexometric titration with standard EDTA solution. The manganese solutions used in obtaining the calibration graph were prepared from this standard manganese solution by dilution with 5*M* ammonium fluoride and water.

RESULTS AND DISCUSSION

Polarographic data for 19 ions in 1*M* ammonium fluoride are shown in Table I and the notes below the table.

The voltammetric oxidation of manganese(II) to manganese(IV) is interesting. Headridge and Taylor[2] have shown that manganese(II) in 0·5*M* hydrofluoric acid–0·5*M* ammonium fluoride can be quantitatively oxidised to manganese(III) with standard permanganate solution. A voltammetric oxidation of manganese(II) to (III) was, therefore, expected. In 0·5*M* hydrofluoric acid–0·5*M* sodium fluoride, the oxidation wave for manganese(II) starts at +0·85 V *vs.* S.C.E. but is not completed before the final rise in current. It could be explained by an irreversible oxidation of manganese(II) to (III), but in 1*M* ammonium fluoride the oxidation is quite definitely to manganese (IV) as shown by the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ value of 28 mV for a reversible two-electron oxidation wave. Cox and Sharpe[3] were able to prepare complex fluorides of manganese(IV) by electrolytic oxidation.

It can be seen from Table I that only vanadium(IV) was expected to interfere with the voltammetric determination of manganese in steel, after a solution of the steel in 1*M* ammonium fluoride had been obtained. To ensure that all of the vanadium was in the +5 state, a slight excess of potassium dichromate was added to the 1*M* ammonium fluoride solutions obtained from steels containing

Table I

Species	$E_{\frac{1}{4}}$, *V vs.* S.C.E.	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$, *mV*
Ferrocyanide	+0·18	56[R]
Silver(I)	+0·21	− 32*
Antimony(V)	+0·34	−122*
Iron(II)	+0·46	185
Iodide	~+0·47[M]	—
Manganese(II)	+0·52	28[R]
Vanadium(IV)	+0·56	158
Thallium(I)	+0·87	95

* Reduction wave.
[R] Reversible wave.
[M] Maximum present which was not suppressed by Triton X-100 (0·004% w/v) or gelatine (0·1% w/v).

The oxidation wave for cobalt(II) started at +0·85 V and was not completed before the final rise in current.

There were no oxidation or reduction waves for antimony(III), arsenic(III) and (V), bromide, chromium(III) or (VI), copper(II), iron(III), nickel(II) and vanadium(V) at potentials >0 V *vs.* S.C.E.

With the rotating platinum electrode in 1*M* ammonium fluoride the final rise in current occurred at +1·1 V *vs.* S.C.E.

The concentration of all ions was 2×10^{-4} *M*.

vanadium. Dichromate oxidises vanadium(IV) to vanadium(V) in 1*M* ammonium fluoride solution but has no effect upon manganese(II).

In 1*M* ammonium fluoride, the limiting current measured at +0·8 V *vs.* S.C.E. was found to be directly proportional to manganese(II) concentration, as expected, in the range $6 \times 10^{-5}M$–$6 \times 10^{-4}M$. The standard deviation of the error in limiting current was 0·18 μA, which corresponds to a relative standard deviation of 1·1% at a manganese concentration of $6 \times 10^{-4}M$. The error in limiting current is expressed by i_L (measured) − i_L (calculated) where the values of i_L (calculated) are points exactly on the straight line calibration graph of limiting current *vs.* concentration.

Method for the analysis of steels or cast irons

Dissolve 0·1 g of alloy of low cobalt content (Note 1) in 10 ml of concentrated hydrochloric acid plus 5 drops (0·25 ml) of concentrated nitric acid. Evaporate the solution just to dryness. Dissolve the residue in 5 ml of concentrated hydrochloric acid and evaporate just to dryness (Note 2). Dissolve the residue in 10 ml of 10*M* hydrofluoric acid and neutralise to pH 6·2 (the pH of 1*M* ammonium fluoride solution) with ammonia solution. Add sufficient 0·1*M* potassium dichromate solution to ensure that the vanadium is entirely in the +5 state, make up the solution to 100 ml in a graduated flask, run the voltammogram, and obtain the concentration of manganese in the solution from a suitable calibration graph. (The authors used the calibration graph mentioned above.)

Note 1. When the cobalt content of an alloy exceeds 10% of the manganese content, the results for manganese are low and the slope of the manganese oxidation wave is less steep than expected. The oxidation wave for cobalt(II) is well separated from that for manganese(II) (see Table I), and should cause no interference with the manganese wave. A possible explanation of the low results is

Table II

Alloy	Mn (certificate), %	Mn (found), %
18/8 stainless steel + Ti BCS 235/1	0·60	0·59, 0·61
Lead steel BCS 212/1	0·91	0·88, 0·91
Hematite cast iron BCS 236/2	1·14	1·14, 1·15
Mn-Mo steel BCS 214/1	1·48	1·48, 1·48
Low alloy steel BCS 251/1	1·54	1·54, 1·54

that cobalt(II) catalyses the aerial oxidation of manganese(II) in 1*M* ammonium fluoride solution. The presence of a manganese(III) fluoride complex in the manganese(II) solution would also explain the decreased slope of the manganese wave. Fortunately many steels contain only very minor amounts of cobalt.

Note 2. To ensure that premature oxidation of manganese(II) does not occur it is necessary to remove nitric acid from the solution before adding hydrofluoric acid.

The results for the determination of manganese in four steels and one cast iron are shown in Table II.

CONCLUSION

The results presented in Table II are considered to be satisfactory. We see no reason why the voltammetric method should not be applied to the determination of manganese in other alloys of low cobalt content. The method should be particularly suitable for the determination of manganese in alloys containing niobium, tantalum and tungsten since the dissolution procedure described above produces clear solutions of these elements in the 1*M* ammonium fluoride base electrolyte.

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Summary—The voltammetric behaviour of 19 ions in 1*M* ammonium fluoride solution has been investigated, using a rotating platinum electrode. In this base electrolyte, manganese(II) is oxidised reversibly to manganese(IV) at +0·52 V *vs.* S.C.E. and this reaction has formed the basis for a simple voltammetric method for the determination of steels and cast iron of low cobalt content.

Zusammenfassung—Das voltametrische Verhalten von 19 Ionen in 1 M Ammoniumfluoridlösung wurde an einer rotierenden Platinelektrode untersucht. In diesem Grundelektrolyten wird Mangan(II) bei +0,52 V gegen die gesättigte Kalomelektrode reversibel zu Mangan(IV) oxydiert. Auf Grund dieser Reaktion wurde eine einfache Methode zur voltametrischen Bestimmung von Mangan in Stählen und Gußeisen von niedrigem Kobaltgehalt entwickelt.

Résumé—On a étudié le comportement voltamétrique de 19 ions en fluorure d'ammonium 1*M*, en utilisant une électrode rotative en platine. Dans cet électrolyte de base, le manganèse (II) est oxydé réversiblement en manganèse (IV) à +0,52 V par rapport à l'électrode de calomel saturée, et cette réaction a constitué la base d'une méthode voltamétrique simple pour le dosage du manganèse dans les aciers et la fonte à faible teneur en cobalt.

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A Titrimetric Study of the Reaction of Quinones in Fluoride Solution with Iron (II)*

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A simple, direct potentiometric titration is described for the determination of the percentage purity of quinones. The quinone, 0·25 to 1 mmole, is dissolved in 50 per cent. v/v aqueous alcoholic solution, which is 0·5 M in hydrofluoric acid and 0·5 M in ammonium fluoride, then titrated with a standardised solution of ammonium iron(II) sulphate. Results are presented for the titration of ten quinones and it has been established that any quinone, which forms part of a couple whose formal electrode potential in the aqueous alcoholic mixed fluoride solution is not less than +0·24 V *versus* the normal hydrogen electrode, can be determined. These quinones include almost all of the 1,4-benzoquinones, 1,2-benzoquinones and phenanthraquinones, many naphthaquinones, but only a few anthraquinones.

QUINONES can be determined in acid solution by titration with standardised solutions of chromium(II), tin(II), titanium(III) and vanadium(II), the quinones being reduced to the corresponding hydroquinones.[1] However, these powerful reducing agents are readily oxidised by oxygen from the air and it is, therefore, necessary to protect these titrants from oxidation by maintaining an inert atmosphere above the solutions at all times. With chromium(II) in particular allowance must be made for a slow reaction between this ion and the hydrated proton. Frequent standardisation of these titrants is, therefore, necessary. A more convenient titrant would be one which is only a mild reductant in the burette but which becomes a powerful reductant when it enters the solution of quinone in the titration vessel.

Iron(II) fulfils these requirements. The iron(II) ion is a mild reducing agent in common acids, the formal electrode potentials of the iron(II) - iron(III) couple being +0·71 V *versus* the N.H.E. in 0·5 M hydrochloric acid and +0·63 V *versus* the N.H.E. in M sulphuric acid.[2] Taylor[3] has, however, reported that the formal electrode potential of the iron(II) - iron(III) couple in aqueous 0·5 M hydrofluoric acid - 0·5 M ammonium fluoride is +0·10 V *versus* the N.H.E., which shows that iron(II) is a much more powerful reductant in this medium. A re-measurement of the potential in the same medium for this study gave a value of +0·12 V *versus* the N.H.E. In 50 per cent. v/v aqueous alcohol, which was 0·5 M in hydrofluoric acid and 0·5 M in ammonium fluoride, the formal electrode potential of this couple is −0·02 V *versus* the N.H.E. Iron(II) is only slightly complexed by fluoride but iron(III) is strongly complexed, and the large drop in potential shown above is the result. The stability constant of the iron(III) fluoride complex will be greater in aqueous alcoholic solution than in aqueous solution and this is reflected in a further drop in formal electrode potential from +0·12 V to −0·02 V *versus* the N.H.E.

These results indicate that many quinones in fluoride solution could be determined by titration with standardised iron(II) solution and a study of these titrations is reported in this paper. Potentiometric end-point determination was used.

The formal electrode potential of the iron(II) - iron(III) couple is also lowered appreciably in the presence of EDTA or phosphoric acid, which also complex iron(III) much more strongly than iron(II). Meites[2] quotes formal electrode potentials of +0·46 V *versus* the N.H.E. and +0·12 V *versus* the N.H.E. for this couple in 2 M orthophosphoric acid and 0·1 M EDTA at pH 4 to 6, respectively. Obviously iron(II) is a more powerful reductant in the presence of fluoride than in phosphoric acid solutions. Iron(II) is also a powerful reductant in the presence of EDTA but this system would be less satisfactory than the fluoride system for the titration of quinones because quinones are less readily reduced in the pH range of 4 to 6 than at pH 3, which was used in this study.

* Paper presented at the Second SAC Conference 1968, Nottingham.

Experimental

Reagents—

Titrant—This was an approximately 0·1 M solution of ammonium iron(II) sulphate in 5×10^{-3} M sulphuric acid.

Solvent for quinones—This was aqueous industrial methylated spirit (50 per cent. v/v), which was 0·5 M in hydrofluoric acid and 0·5 M in ammonium fluoride.

Quinones—1,4-Benzoquinone, 2,6-dimethyl-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and tetrachloro-1,2-benzoquinone were obtained from Aldrich Chemical Company; methyl-1,4-benzoquinone, 2,6-dichloro-1,4-benzoquinone and 1,4-naphthaquinone-2-sulphonic acid potassium salt from Eastman Kodak; 1,2-naphthaquinone-4-sulphonic acid sodium salt and 9,10-phenanthraquinone from B.D.H.; and tetrahydroxy-1,4-benzoquinone from Koch-Light Laboratories. The 1,4-benzoquinone was recrystallised twice from light petroleum (boiling range 60° to 80° C). Tetrahydroxy-1,4-benzoquinone was recrystallised from water. The other quinones were used as received from the suppliers.

Potentiometric titrations were carried out in the usual way in a glass cell with two compartments separated by a No. 4 porosity glass sinter backed by a plug of gel consisting of saturated aqueous sodium fluoride solution, 2 per cent. w/v in agar. The reference electrode compartment contained a saturated calomel electrode. The solution compartment had a capacity of 330 ml. The indicator electrode was constructed from a 20 cm length of 26-gauge platinum wire sealed into a 12·5 cm length of 6-mm bore polythene tubing. The 5 cm of wire protruding at the lower end was wound into a spiral for immersion in the solution. A polythene lead-in tube was used to pass oxygen-free nitrogen through the solution when the potential difference in the cell was not being measured.

Method for determination of quinones—

Place 100 ml of the aqueous alcoholic mixed fluoride solution in the titration cell and pass a steady stream of nitrogen through the solution. Weigh accurately 0·25 to 1 mmole of the quinone and transfer this to the titration cell by washing with a further 100 ml of the mixed fluoride solution. Continue bubbling nitrogen, which serves to provide an inert atmosphere above the solution, to mix the solution and to displace any dissolved oxygen.

Stop the flow of nitrogen and measure the cell potential. Re-start the flow of nitrogen and run in ammonium iron(II) sulphate solution until about half of the quinone is reduced. Allow 30 seconds for mixing, stop the flow of gas and measure the potential. Repeat this procedure making further additions of titrant, the amounts of titrant added being smaller as the expected end-point is approached, until 0·1-ml additions are made in the vicinity of the end-point. Continue the titration for several millilitres past the end-point until the fall in potential after each addition of titrant is small, then plot a graph of working electrode potential against the volume of titrant added. Read off the equivalence-point from the straight portion of the graph. For the quinone - iron(II) reaction, which is a 2 to 1 electron change, the equivalence-point is at the potential which is one third of the way between the formal electrode potentials of the quinone - hydroquinone and iron(II) - iron(III) couples.[4]

Standardise the ammonium iron(II) sulphate solution by titrating a known weight of recrystallised 1,4-benzoquinone in aqueous alcoholic mixed fluoride solution by the above method.

Results and discussion

Blank determinations were carried out to ascertain whether other reducible species were present in the quinone solution. The results of these determinations are as follows: 1·000 mmole of 1,4-benzoquinone *plus* 200 ml of aqueous alcoholic mixed fluoride solution required 20·17 ml of approximately 0·1 M ammonium iron(II) sulphate solution (mean of two titrations); 0·500 mmole of 1,4-benzoquinone *plus* 200 ml of aqueous alcoholic mixed fluoride solution required 10·10 ml of 0·1 M ammonium iron(II) sulphate solution (mean of two titrations). Hence by subtraction 0·500 mmole of 1,4-benzoquinone required 10·07 ml of 0·1 M ammonium iron(II) sulphate solution, which gave a blank of 0·03 ml for the 200 ml of aqueous alcoholic mixed fluoride solution. This showed that there was an insignificant amount of reducible material present in the alcohol, water, hydrofluoric acid and ammonium fluoride and no further blank determinations were made. Any dissolved oxygen in the ammonium iron(II) sulphate solution will be reduced by the iron(II) as soon as the titrant enters the fluoride solution and is allowed for in the standardisation of the iron(II) solution with 1,4-benzoquinone.

The relative standard deviation for the titration of ten 1·000-mmole amounts of 1,4-benzoquinone with the same ammonium iron(II) sulphate solution was 0·9 per cent. Results of the titration of ten quinones, including the determination of the percentage purity of these materials, are shown in Table I.

TABLE I

POTENTIOMETRIC TITRATION OF QUINONES

Quinone	Amount taken, mmoles*	Titres on sample solutions, ml	Titres on 1·000 mmole of 1,4-benzoquinone, ml	Purity, average per cent.	Average fall in potential, mV†
1,4-Benzoquinone	1·000	—	20·30, 20·40, 20·00, 20·10, 19·90, 20·20, 19·85, 20·25, 20·00, 20·50	Taken as 100·0	470
Methyl-1,4-benzoquinone	1·000	20·40, 20·20, 20·40, 20·35, 20·20, 20·20	20·20, 20·25, 20·40, 20·30, 20·30	100·0	430
2,6-Dimethyl-1,4-benzoquinone	1·000	19·90, 19·80, 20·10	20·10, 19·90, 19·90	99·8	325
1,3-Dichloro-5,6-dicyano-1,4-benzoquinone	1·000	19·40, 19·40, 19·10	20·15, 20·00, 20·10	96·1	300
Tetrahydroxy-1,4-benzoquinone	1·000	3 titres of approximately 17·5‡	20·35, 20·30, 20·15	approximately 82	120
2,6-Dichloro-1,4-benzoquinone	0·250	4·65, 4·55	5·30, 5·30	86·8	420
Tetrachloro-1,2-benzoquinone	0·250	4·60, 4·75	4·90, 4·90, 5·20	93·5	500
1,2-Naphthaquinone-4-sulphonic acid sodium salt	1·000	19·70, 19·80, 20·10	19·90, 20·00, 20·40	98·9	380
1,4-Naphthaquinone-2-sulphonic acid potassium salt	1·000	19·70, 20·20, 20·20, 19·60	20·15, 20·00, 20·10, 20·35, 20·40, 20·30	98·2	325
9,10-Phenanthraquinone	0·250	5·00, 5·15, 5·10	5·20, 5·25	97·2	150

* 1·000 millimole of quinone was taken unless this amount was not soluble in 200 ml of mixed fluoride solution. Then 0·250 millimole was taken.

† The fall in potential was that between the readings for 2 ml on either side of the end-point for determinations carried out on 1 millimole of quinone and 0·5 ml on either side of the end-point for determinations on 0·25 millimole of quinone.

‡ Because of the relatively low fall in potential of the working electrode, it was not possible to determine this end-point precisely.

It was evident that an end-point determination could not be made if the fall in potential, as defined previously was less than 100 mV. If the fall in potential was between 100 and 150 mV only an approximate end-point could be determined from the potentiometric titration

TABLE II

COMPARISON OF THE FORMAL ELECTRODE POTENTIALS OF QUINONE - HYDROQUINONE COUPLES IN AQUEOUS ALCOHOLIC SOLUTIONS

Quinone	$E^{O'}_{TS}$ (V *versus* N.H.E.)	$E^{O'}_{C}$ (V *versus* N.H.E.)
1,4-Benzoquinone	0·50	—
Methyl-1,4-benzoquinone	0·46	0·66 (50)
2,6-Dimethyl-1,4-benzoquinone	0·40	*
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	0·31	—
Tetrahydroxy-1,4-benzoquinone	0·17	—
2,6-Dichloro-1,4-benzoquinone	0·53	0·75 (95)
Tetrachloro-1,2-benzoquinone	0·66	0·87 (50)
1,2-Naphthaquinone-4-sulphonic acid sodium salt	0·43	0·64 (50)
1,4-Naphthaquinone-2-sulphonic acid potassium salt	0·36	0·56 (50)
9,10-Phenanthraquinone	0·24	0·47 (95)

* No published results were available for this quinone but $E^{O'}_{C}$ for 2,3-dimethyl-1,4-benzoquinone is 0·59 V in aqueous and and in aqueous alcoholic solution (50 per cent. v/v), and $E^{O'}_{C}$ for 2,5-dimethyl-1,4-benzoquinone is 0·60V in aqueous solution.

curves. However, if the fall in potential exceeded 150 mV, the end-point could be determined with good precision. The potential of the working electrode attained a steady value within 30 seconds.

The average formal electrode potentials of the quinone - hydroquinone couples for the various quinones determined in this study are compared in Table II with potentials reported by Clark.[5] $E^{0'}_{TS}$ is the formal electrode potential as determined in this study for the quinone - hydroquinone couple in aqueous alcohol (50 per cent. v/v), which is 0·5 M in hydrofluoric acid and 0·5 M in ammonium fluoride. $E^{0'}_{C}$ is the formal electrode potential as reported by Clark for the quinone - hydroquinone couple in aqueous alcoholic solution at pH 0. The values in parentheses in the third column are the percentages of alcohol (v/v) in the solutions.

The formal electrode potentials reported from this study were read from the working plots at the titration value half of that at the end-point, and 0·24 V, the potential of the saturated calomel electrode at 20° C, was added to the readings to obtain the formal electrode potentials of the quinone systems relative to the normal hydrogen electrode.

It will be noticed that the values of $E^{0'}_{TS}$ are about 0·2 V less positive than those of $E^{0'}_{C}$. This is to be expected as a result of the differences in hydrogen-ion activity in each solution. For aqueous solutions, it can be readily calculated that the formal electrode potentials of quinone - hydroquinone couples in 0·5 M hydrofluoric acid - 0·5 M ammonium fluoride (pH 3·15) will be about 0·19 V more negative than the formal electrode potentials of these couples at pH 0.

A comparison of the results in Table II with results reported by Clark[5] for many other quinone - hydroquinone couples shows that the method described above should be satisfactory subject to solubility for the direct titrimetric determination of any quinone that forms part of a couple whose formal electrode potential in the aqueous alcoholic mixed fluoride solution is not less than +0·24 V *versus* the N.H.E., or whose formal electrode potential in aqueous or aqueous alcoholic solution at pH 0 is not less than +0·45 V *versus* the N.H.E. These include almost all 1,4-benzoquinones, 1,2-benzoquinones and phenanthraquinones, many naphthaquinones, but only a few anthraquinones.

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THE APPLICATIONS OF HYDROFLUORIC ACID AND FLUORIDES IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION

For a long time hydrofluoric acid was not as widely used in analytical chemistry as hydrochloric, nitric, or sulfuric acids. This was partly because it is both a moderately weak and non-oxidizing acid, having a pK_a-value of 2.9 in 0.5 *M* sodium perchlorate. Other deterrents to its use have been the facts that it attacks glassware and that, particularly when concentrated, it produces nasty burns when brought into contact with the skin.

Nowadays, however, the ready availability of laboratory ware made from such materials as polyethylene, polypropylene, and Teflon® (polytetrafluoroethylene) makes it easy to solve the perennial problem of finding containers for the acid, and makes it possible to take advantage of certain unique and analytically advantageous properties of hydrofluoric acid and fluorides.

Under the proper conditions, which will be discussed later, hydrofluoric acid is a very convenient solvent for silicates, since it reacts with them to form the stable water-soluble fluosilicate anion. Indeed this use of the acid was mentioned by the Swedish chemist Bergman (1735 to 1784).[1] Solutions containing hydrofluoric acid are also useful solvents for species such as zirconium (IV), niobium (V), tantalum (V), and tungsten (VI), which also form stable and soluble fluoro complexes.

Because hydrogen fluoride is very volatile (boiling at 19° C), it is used as a concentrated

aqueous solution. Commercial hydrofluoric acid is an approximately 48% (w/v) solution. Since hydrofluoric acid is a relatively weak acid, many fluoro complexes are at least partly dissociated in strong acids such as hydrochloric or sulfuric acid. However some fluoro complexes, such as those of titanium (IV), zirconium (IV), and niobium (V), are very stable and persist even in the presence of strong acids. Because hydrofluoric acid volatilizes from aqueous solutions at about 110° C, these complexes can be broken down by heating strongly with perchloric or, preferably, sulfuric acid. Prolonged heating is essential if the last traces of fluoride are to be removed. The fluorides most widely used in analytical chemistry are those of ammonium, sodium, and potassium.

Since hydrofluoric acid and fluorides are mainly used in analytical chemistry because of their complexing ability, the next section of this review deals with the stability of fluoride complexes.

There have been no startling advances in the uses of hydrofluoric acid and fluorides during the past 20 years, but progress has been steady. Their uses fall into 5 categories. First, the unique properties of aqueous solutions containing hydrofluoric acid as solvents have already been mentioned. There has been much activity in this field within the last decade, particularly with Teflon®-lined bombs used at temperatures in excess of 110° C. Second, the use of fluoride ion as a complexing agent has been exploited in the development of separation procedures such as ion-exchange and partition chromatography and solvent extraction, of which the last is sometimes followed by absorption spectrophotometric determination of the extracted element. The fundamental advances in these fields were made between 1945 and 1965; since then most of the progress that has been made has involved the improvement of existing methods rather than the development of new ones. Third, fluoride ion is used as a precipitant for certain cations, with which it forms insoluble salts. This is a long-established use of fluorides, but because gravimetric methods are being replaced by faster instrumental ones there is little activity in this area at the present time. Fourth, like all complexing agents, fluoride has a profound effect on the formal potentials of certain redox couples, and these effects have been used to develop methods for the determination of many elements by titration, polarography, and so on. This is a field in which there was much interest in the 1960s. Finally, there have been a number of miscellaneous applications of fluoride ions; these include its use as a masking agent and as a reagent to improve the sensitivity with which elements such as zirconium and tantalum can be determined by atomic absorption spectroscopy. All of these fields are reviewed in the following pages.

II. THE STABILITIES OF FLUORIDE COMPLEXES

A. Stability Constants

The fluoride ion is the smallest of the halide anions, having an ionic radius of 1.33 Å and it is not readily polarized. It coordinates most readily with cations of high charge and small radius, the bonding in many instances being mainly electrostatic in nature. These considerations alone would account for the formation of strong fluoride complexes in aqueous solution by Be^{2+}, (B^{3+}), Al^{3+}, Ga^{3+}, In^{3+}, (Si^{4+}), Sn^{2+}, (Sn^{4+}), Sc^{3+}, Y^{3+}, (Ti^{4+}), (Zr^{4+}), Th^{4+}, (V^{5+}), (Ta^{5+}), Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}. This is borne out by the stepwise stability or formation constants of fluoride complexes shown in Table 1. This information is reproduced from the Chemical Society's publication on "Stability Constants".[2] In the list shown, the species in parenthesis are, of course, partly or completely hydrolyzed in aqueous solutions in the absence of complexing agents.

The stability constants for the monofluoro complexes of many elements are shown more clearly for comparison in Figure 1. Most of these were taken from Table 1, but a few have been estimated mostly from the data of Babko.[3]

Equilibrium data for the formation of the fluoro complexes of several metallic ions have been presented by Goldstein[4] in the form of useful distribution diagrams. These are plots of fraction of each species present versus fluoride concentration.

B. Inhibition of Hydrolysis

One of the most useful properties of the fluoride ion is its ability to complex with inorganic species such as silicon (IV), zirconium (IV), niobium (V), and tungsten (VI) to form soluble fluoro complexes. These species have high affinities for the hydroxyl ion, whose ionic radius is similar to that of the fluoride ion. Because the hydroxyl ion frequently acts as a bridging ligand, the resulting hydroxide complexes tend to poly-

TABLE 1

Stepwise Stability Constants of Fluoride Complexes

Species	Medium*	Temp.(°C)	Stepwise Stability Constants†
Be^{2+}	0.5 NH_4ClO_4	25	K_1 4.7, K_2 3.6, K_3 2.8, K_4 2.3
Al^{3+}	0.53 KNO_3	25	K_1 6.1, K_2 5.0, K_3 3.9, K_4 2.7, K_5 1.6, K_6 0.5
Ga^{3+}	var	20	K_1 4.5, K_2 3.8, K_3 2.8, K_4 1.5, K_5 0.3
In^{3+}	1 $NaClO_4$	25	K_1 3.7, K_2 2.6, K_3 2.3, K_4 1.1
Tl^{+}	0 corr	25	K_1 0.1
Si^{4+}	0.5 HCl		K_6 4.0
Ge^{4+}	0.5 HCl		K_6 3.9
Sn^{2+}	0.85 $NaClO_4$	25	K_1 6.3, K_2 2.5, K_3 0.5
Pb^{2+}	1 $NaClO_4$	25	K_1 1.5
Bi^{3+}	1.89 $HClO_4$	25	K_1 4.7, K_2 3.6
Sc^{3+}	0.5 $NaClO_4$	25	K_1 6.2, K_2 5.3, K_3 4.1, K_4 2.9
Y^{3+}	0.5 $NaClO_4$	25	K_1 3.9, K_2 3.2, K_3 3.2
La^{3+}	0.5 $NaClO_4$	25	K_1 2.7
TiO^{2+}	3 $NaClO_4$	25	$K_1 > 5.4$, K_2 4.4, K_3 4.0, K_4 3.7
Zr^{4+}	0 corr	25	K_1 9.8
	1 $NaClO_4$	25	K_4 2.8, K_5 1.9, K_6 1.4
Th^{4+}	0 corr	25	K_1 8.7
VO^{2+}	1 $NaClO_4$	20	K_1 3.3, K_2 2.3, K_3 1.6, $K_4 \sim 0.7$
Ta^{5+}	1(H,Na)ClO_4	25	K_5 4.8, K_6 3.6, K_7 3.3, K_8 3.0, K_9 3.6
Pa^{5+}	1 $NaClO_4$	25	K_1 5.4, K_2 5.0, K_3 4.9, K_4 4.8, K_5 4.5, K_6 4.4, K_7 3.7, K_8 1.7
Cr^{3+}	0.5 $NaClO_4$	25	K_1 4.4, K_2 3.3, K_3 2.5
Mn^{2+}	1 $NaClO_4$	25	K_1 0.8
Fe^{3+}	0.5 $NaClO_4$	25	K_1 5.2, K_2 3.9, K_3 2.9
	var		K_4 2.0, K_5 0.4
Ni^{2+}	0.5 $NaClO_4$	15	K_1 0.7
Ag^{+}	0 corr	25	K_1 0.4
Zn^{2+}	2 $NaClO_4$	25	K_1 0.9
Cd^{2+}	1 $NaClO_4$	25	K_1 0.5, K_2 0.1
Hg_2^{2+}	0 corr	25	$K_1 < 0.5$
Hg^{2+}	0 corr	25	K_1 0.1
U^{4+}	2 $HClO_4$		K_1 7.2, K_2 5.3
	0.12 $HClO_4$	25	K_3 4.2, K_4 4.3, K_5 1.6, K_6 2.3
UO_2^{2+}	1 $NaClO^4$	20	K_1 4.6, K_2 3.3, K_3 2.6, K_4 1.4
Pu^{4+}	0 corr	25	K_1 7.9

*The number before the salt is concentration which in the original paper is usually expressed in mole l^{-1} (M), but occasionally as mole kg^{-1} (m).

The entry 'var' means that the ionic strength was varied.

The entry '0 corr' means that the constant(s) have been corrected to zero ionic strength.

†The numbers given are the logarithms to the base 10 of the appropriate equilibrium constant. For example, 'K_1 5.9' means 'log K_1 = 5.9.'

(From *Stability Constants*, Special Publication No. 17, The Chemical Society, London, 256. With permission.)

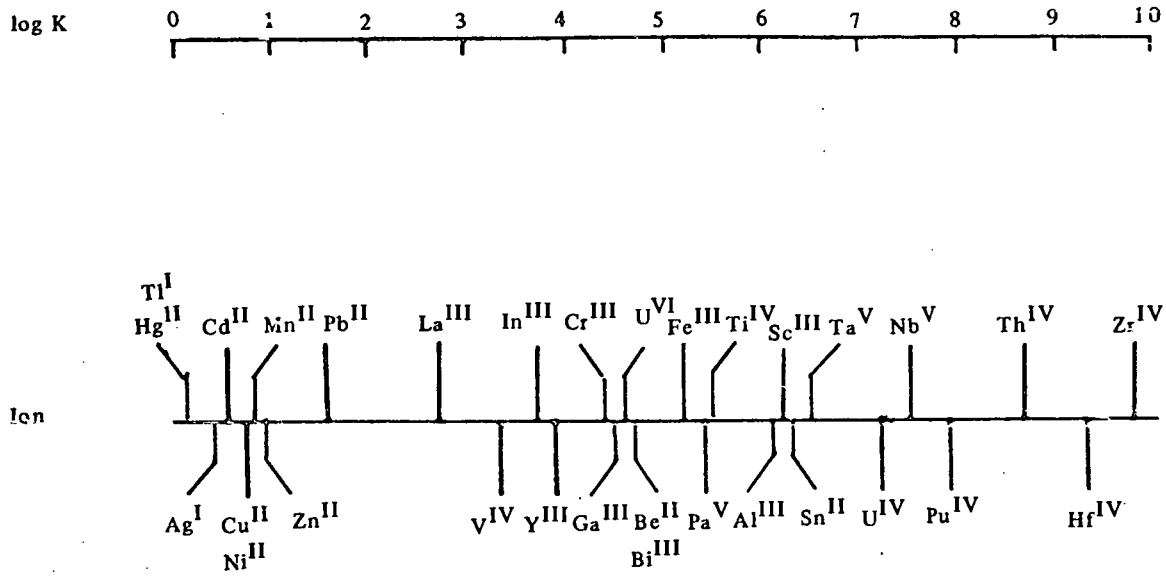

FIGURE 1. Stability constants of some monofluoride complexes. The values of log K for titanium(IV), tantalum(V), niobium(V), and hafnium(IV) have been estimated.

merize readily, and precipitation will result if the polymerization number becomes sufficiently high. In the presence of fluoride ion, this hydrolytic polymerization is inhibited because hydroxyl ions in coordination positions are replaced by fluoride ions, which are much less effective bridging ligands than hydroxyl ion.

Therefore, it is frequently desirable to add hydrofluoric acid to solutions of silicon (IV), zirconium (IV), hafnium (IV), niobium (V), tantalum (V), or tungsten (VI) so that these may be retained in true solution prior to separating them or determining them by techniques such as solvent extraction, ion-exchange chromatography, titrimetry, and atomic absorption spectroscopy.

III. THE DISSOLUTION OF MATERIALS IN FLUORIDE MEDIA

A. Decomposition using Hydrofluoric Acid

1. Metals

Easily oxidized metals such as magnesium and zinc readily dissolve in hydrochloric acid, while more noble metals such as copper, mercury, and platinum are dissolved by nitric acid alone or together with hydrochloric acid. However, nitric acid will not dissolve zirconium, hafnium, niobium, and tantalum. Fortunately, these elements form very stable fluoro complexes and may be conveniently dissolved by a mixture of hot hydrofluoric and nitric acids. In fact, they will dissolve slowly in hydrofluoric acid alone. The presence of hydrofluoric acid in the dissolving medium is also particularly useful for the dissolution of metallic samples containing tungsten, for a soluble fluotungstate complex is produced. In the absence of such a complexing agent the tungsten is converted to insoluble tungstic acid.

When the metal to be analyzed also contains appreciable amounts of niobium or tantalum, it is common practice to add hydrofluoric acid to the acid mixture used in dissolving the metal. However, only a few examples will be quoted to illustrate these points. Nickel-base[5] and cobalt-base[6] alloys have been analyzed for major alloying elements including niobium, tantalum, and tungsten by atomic absorption spectroscopy after dissolving the alloys in a mixture of acids including hydrofluoric acid. Headridge and Taylor[7] dissolved ferrotungsten in a mixture of hydrofluoric acid, hydrochloric acid, and hydrogen peroxide as the first step in a method for the titrimetric determination of the iron, tungsten, and molybdenum contents. Kakita and Goto[8] dissolved niobium metal or ferroniobium in a mixture of hydrofluoric and nitric acids in a method for the spectrophotometric determination of tantalum in these matrices.

Langmyhr and Paus[9] have determined silicon, aluminum, magnesium, calcium, titanium, manganese, chromium, copper, nickel, cobalt, lead, and tin in ferrosilicon by atomic absorption

spectroscopy after dissolving the material in hydrofluoric and nitric acids in a Teflon®-lined bomb by heating at 110° C for 30 min. Further details on such bombs are given in Section III A3 of this review, dealing with silicates and other minerals. Price and Roos[10] have also employed hydrofluoric acid in determinations of silicon by atomic absorption spectroscopy in cast irons and aluminum alloys. In the presence of this acid, silicon is held in solution as the fluosilicate anion.

2. Oxides, Carbides, Nitrides, and Borides.

Hot hydrofluoric acid is also very useful for dissolving the oxides of titanium, zirconium, hafnium, niobium, and tantalum, although the time that is required to effect solution depends on the previous heat treatment that the oxide has received. An oxide that has been heated for a long period at temperatures above 1,000° C takes longer to dissolve than one that has been dehydrated at lower temperatures. Willard and Rulfs[11] have stated that a mixture of hydrofluoric and nitric acids will dissolve the carbides of titanium, zirconium, niobium, tantalum, and tungsten; the nitrides of titanium, zirconium, niobium, and tantalum; and the borides of zirconium and probably titanium, niobium, tantalum, and tungsten. Nitric acid alone would decompose these compounds much less readily.

3. Silicates and Other Minerals.

Hydrochloric, nitric, and perchloric acids decompose silicates containing high proportions of the alkali and alkaline earth elements. However, silicates containing only small proportions of elements with basic oxides are not appreciably attacked by these acids. On the other hand, hydrofluoric acid is most useful for decomposing many silicate minerals. This is so because silicon(IV) reacts with fluoride to form the stable fluosilicate anion, SiF_6^{2-}, and other constituents of many silicate rocks, such as iron(III) and aluminum, also form stable fluoro complexes. Heating with hydrofluoric acid speeds up the decomposition process, and Langmyhr and Sveen[12] have shown that the decompositions of quartz (SiO_2), staurolite ($FeAl_4Si_2O_{10}(OH)_2$), and epiodote ($Ca_2(Al,Fe)_3(SiO_4)_3OH$) are as effective with hydrofluoric acid alone as with its mixtures with hydrochloric, sulfuric, and perchloric acids. Dissolution of silicate minerals with hydrofluoric acid, either alone or in mixtures with other acids, usually leads to the formation of precipitates of slightly soluble fluorides or complex fluorides. These are readily brought into solution by adding an excess of aluminum ions. An extensive review of the use of hydrofluoric acid in the decomposition of minerals has been written by Doležal, Povondra, and Šulcek.[13]

It has been shown that there is no loss of silicon as volatile silicon tetrafluoride when silica is dissolved in concentrated hydrofluoric acid, even at 100° C, if an appreciable volume of solution is maintained.[14] However, the solution must not be evaporated to small volume or loss of silicon does occur. Evaporation of solutions containing silicon in the presence of hydrofluoric acid and higher-boiling acids such as sulfuric or perchloric acid does, of course, result in the loss of silicon as the tetrafluoride. When silicon in hydrofluoric acid solution is to be determined spectrophotometrically, the fluosilicate anion can be dissociated and fluoride ion bound by adding an excess of aluminum ions, the stable fluoaluminate ion being produced.

However, it must be stressed that there are numerous silicates that are not decomposed entirely by treatment with hot hydrofluoric acid or with acid mixtures containing hydrofluoric acid in an open beaker. Willard and Rulfs[15] state that kyanite (Al_2SiO_5), beryl ($Be_3Al_2Si_6O_{18}$), zircon ($ZrSiO_4$), topaz ($Al_2F_2SiO_4$), andalusite (Al_2SiO_5), and some tourmalines ($XY_3B_3Al_3[(Al,Si)_3O_9]_3(OH,F)_4$, where X = Na, Ca and Y = Mg, Fe, or Li) are resistant to such treatment.

When minerals are decomposed in boiling hydrofluoric acid certain elements can be lost partially as volatile fluorides. These include boron, arsenic, and selenium(IV). From a mixture of perchloric and hydrofluoric acids at 200°C, boron, silicon, and arsenic are lost entirely by volatilization and varying amounts of germanium, antimony, chromium, selenium, manganese, and rhenium are lost as well.[16] When silicates are decomposed with a mixture of nitric and hydrofluoric acids, no loss of selenium occurs,[17] presumably because selenium(VI) is formed and is nonvolatile. The loss of boron through volatilization as boron trifluoride during the dissolution of silica in hot hydrofluoric acid is prevented by the addition of mannitol.[18]

When hydrofluoric acid alone or in mixtures with other acids is used to decompose minerals,

very stable fluoro complexes of elements such as titanium and zirconium are produced. It is essential to dissociate these compounds and remove fluoride from the solution before determining these elements spectrophotometrically. This is usually done by adding sulfuric acid if it is not already present and evaporating the solution to dense white fumes of sulfur trioxide. Strong heating is necessary to remove all fluoride and it is often advisable, after obtaining the first fumes of sulfur trioxide, to cool the beaker or crucible, wash down the side with a little water, and reheat until sulfur trioxide is again evolved. Indeed, in order to expel the last traces of fluoride, Langmyhr[12] reports that it is necessary to evaporate twice, not only to dense fumes of sulfur trioxide, but to complete dryness at a final temperature of 280±10° C.

Of course, the volatilization of silicon tetrafluoride from a strongly heated mixture of hydrofluoric and sulfuric acids is the method used for removing silica from a silica precipitate before recovering the small amount of mixed oxides that accompanies silica in the wet chemical method for the analysis of a silicate. It is also used to remove the small amount of silica accompanying the mixed oxides in this classical method.

For the determination of iron(II) in silicates, decomposition with hydrofluoric acid is particularly useful. Since hydrofluoric acid is a nonoxidizing acid, the iron(II) passes unchanged into solution, where it can be subsequently titrated with a standard solution of an oxidizing agent or determined spectrophotometrically.[19] However the formal potential of the iron(III)/iron(II) couple is so far displaced toward less positive values in the presence of hydrofluoric acid, which strongly complexes iron(III), that iron(II) may be readily oxidized by oxygen from the air. For this reason the decomposition is best carried out under an inert atmosphere.

Alternatively, the rock sample can be decomposed by hydrofluoric acid in the presence of a known excess of oxidizing agent, such as vanadate, dichromate, or permanganate, which oxidizes iron(II) to iron(III). The excess of oxidant can then be determined by titration. This method is inapplicable in the presence of sulfide. In rocks iron(II) can also be determined by decomposing the rock with boiling hydrofluoric and sulphuric acids in the presence of potassium iodate.[20] Iodine, the reduction product, is volatile in the steam and is removed. The unreacted iodate is determined by adding excess iodide and titrating of the resulting iodine with standard sodium thiosulfate solution. The decomposition can be carried out in a Pyrex® flask.

Minerals of niobium and tantalum, with the exception of the rare simpsonite ($Al_2Ta_2O_8$), are decomposed by heating with a mixture of hydrochloric and hydrofluoric acids under mild pressure.[21] This is done by adding the sample and acid mixture to a polyethylene beaker, which is then covered with a piece of thin polyethylene sheet held tightly against the outside of the beaker with a rubber band. The beaker is heated on a steam bath for about 2 hr with occasional mixing by swirling. Zircon is not attacked, and cassiterite (SnO_2) is only slightly attacked, by this treatment.

It was stated earlier that certain silicate minerals are not completely decomposed by hot hydrofluoric acid, alone or in a mixture with another acid, in an open beaker. Ito[22] has achieved very effective decomposition by heating samples for 3 to 4 hr at 240°C in a Teflon® liner in a stainless steel bomb, using equal volumes of 1:1 sulfuric acid and 48% hydrofluoric acid. His work was directed toward the determination of iron(II) by titration of the final solution with standard permanganate and the determination of alkalis by flame photometry. Complete decomposition occurred with tourmaline, axinite ($H(Ca,Fe,Mn)_3Al_2B(SiO_4)_4$), and staurolite, as well as with more easily decomposed minerals. The minerals named were incompletely decomposed by conventional acid attack in an open beaker. Nonsilicate minerals are often difficult to dissolve in acids and a longer period of heating (up to 16 hr) is required to decompose them completely even in the Teflon® bomb. With the above acid mixture in the bomb, complete decomposition has been achieved with magnetite ($FeO \cdot Fe_2O_3$), ilmenite ($FeO \cdot TiO_2$), chromite ($FeO \cdot Cr_2O_3$), columbite and tantalite ($(Fe,Mn)(Ta,Nb)_2O_6$), baddeleyite (ZrO_2), rutile (TiO_2), and corundum (Al_2O_3). Zircon is only partly decomposed with the mixed acids but decomposes completely when heated for 10 hr at 240° C with hydrofluoric acid alone. Pyrite (FeS_2) is only partly decomposed.

Langmyhr and Sveen[12] have carried out further work on the decomposition of minerals using a 1:1 (v/v) mixture of concentrated hydrofluoric and perchloric acids for 1 hr in a Teflon®-lined aluminum bomb at 250 ± 10° C. Certain minerals

that do not decompose on heating in an open beaker are decomposed in the bomb. These include beryl, kyanite, staurolite, pyrite, chalcopyrite ($CuFeS_2$), and pyrrhotite (Fe_nS_{n+1}). Topaz was only partially decomposed by this treatment.

May and Rowe[23] have also used a metal bomb containing a removable Nichrome-cased platinum crucible to decompose samples of minerals with hydrofluoric acid or with a mixture of hydrofluoric and sulfuric acids. Temperatures of 400 to 450° C and pressures as high as 6000 psi could be maintained for 24 hr. Complete decomposition was achieved for minerals such as zircon, which are not decomposed in open beakers at the boiling point of the acid. The great advantage of Teflon®-lined bombs is that elements with volatile fluorides such as silicon tetrafluoride are unable to escape from the bombs and subsequently may be determined spectrophotometrically or by other means. This is particularly useful in the case of silicon.

As a preliminary step in analyses by atomic absorption spectroscopy, Langmyhr and Paus[24] have decomposed silicate rocks by treatment with hydrofluoric acid, either at about 100° C, in plastic bottles or, for more resistant materials, in a Teflon®-lined bomb at 150 to 250° C. They describe a general procedure to be adopted when nothing is known about the ease of decomposition of the material to be analyzed. An atomic absorption finish has been used to determine silicon, aluminum, total iron, magnesium, calcium, sodium, potassium, titanium, and manganese. Any insoluble fluorides or fluoro complexes that remain after the decomposition procedure are brought into solution by heating with boric acid.

In an important series of papers, hydrofluoric acid decomposition procedures and atomic absorption spectroscopic finishes have also been described by these authors for the determination of many elements in a wide variety of materials. These determinations are listed in Table 2.

Bernas[32] has also reported on the decomposition of samples of granite, diabase, and tektite by treatment with aqua regia and hydrofluoric acid in a Teflon®-lined vessel at 110°C, followed by treatment with excess of boric acid to dissolve insoluble fluorides and determination of silicon, iron, aluminum, titanium, vanadium, calcium, magnesium, sodium, and potassium by atomic absorption spectroscopy.

B. Decomposition Using Fused Potassium Hydrogen Fluoride or Ammonium Fluoride

Potassium hydrogen fluoride or ammonium hydrogen fluoride may be used as a flux for the decomposition of minerals containing elements such as beryllium, zirconium, niobium, tantalum, and silicon, which form very stable complexes with fluoride ion. A good account of the use of these fused fluorides as reagents for the decomposition of minerals is given by Doležal and co-workers.[33] Fusion with these reagents should be made in platinum crucibles.

Potassium hydrogen fluoride melts at 239° C

TABLE 2

The Determinations of Elements in Various Materials by Atomic Absorption Spectroscopy after Decomposition with Hydrofluoric Acid

Material analyzed	Elements determined	Ref.
Silica	Al, Fe, Mg, Ca, Ti	25
Bauxite	Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, Cr	26
Cements, clinkers, raw mixes, and siliceous limestones	Si, Al, Fe, Ca	27
Iron ores	Si, Al, Mg, Ca, Na, K, Ti, Mn	28
Slags	Si, Al, Fe, Mg, Ca, Ti, Mn, Cr, V	28
Felspars	Si, Al, Fe, Mg, Ca, Na, K	29
Silicate minerals and rock reference samples	Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn	30
Sulfide minerals and ores	Fe, Pb, Si, Al, Mg, Ca, Na, K, Ti, Mn, Zn, Cu	31

and readily loses hydrogen fluoride when heated. Since the presence of hydrogen fluoride is essential in the decomposition process, it is necessary to mix the powdered mineral intimately with excess potassium hydrogen fluoride and to heat the mixture very slowly so as to give time for the hydrogen fluoride to attack the mineral matrix. The temperature of the crucible and contents is therefore raised very slowly to a dull red heat over a period of 15 min, after which decomposition of the mineral should be complete. Silicon is lost as volatile silicon tetrafluoride during the fusion. Minerals that are decomposed by this attack include beryl,[34] niobates, tantalates, and zircon.[33] It seems likely that other elements forming volatile fluorides, such as arsenic and boron, will be lost along with silicon tetrafluoride. With this fusion care must also be taken not to heat too strongly when elements that form somewhat less volatile fluorides are present. These include molybdenum, tantalum, and niobium.[35]

With the object of determining thoria, monazite sands have been decomposed by fusion with potassium hydrogen fluoride.[36] Insoluble rare earth and thorium fluorides were separated by centrifugation and then brought into solution by treatment with saturated aluminum nitrate solution. Thorium was separated from the rare earths by solvent extraction and determined spectrophotometrically.

Silicates that are resistant to decomposition by boiling acids, such as topaz and kyanite, can be decomposed by fusion with ammonium fluoride.[37] According to Erdey et al.,[38] ammonium fluoride decomposes on heating, yielding ammonium hydrogen fluoride with the evolution of ammonia, the rate of the reaction being greatest at 145° C. The ammonium hydrogen fluoride then decomposes to ammonia and hydrogen fluoride, the rate of this decomposition being greatest at 225° C. Ammonium hydrogen fluoride melts at 125° C with decomposition beginning at 80° C and reaching a maximum rate at 235° C.

IV. ION-EXCHANGE SEPARATIONS AND PARTITION CHROMATOGRAPHY

A. Ion-Exchange Separations

Since many elements form stable fluoro complexes, which are usually anionic in the presence of excess fluoride, it is understandable that extensive studies have been made on the separation of elements on columns of ion-exchange resins from solutions containing fluoride. Anionic fluoro complexes are usually absorbed from fluoride solutions on strongly basic anion-exchange resins, but elements that either do not form fluoro complexes or form only cationic or neutral fluoro complexes are not held strongly by the resin. On strongly acidic cation-exchange resins, uncomplexed cations and cationic fluoro complexes are generally held while neutral and anionic fluoro complexes are not absorbed.

Much pioneering work on the separation of elements on columns of ion-exchange resins was undertaken by Kraus and co-workers in the late 1940s and 1950s. Their early investigations included the separations of niobium and tantalum[39] and of niobium and zirconium[40] from hydrochloric acid - hydrofluoric acid media on the anion-exchange resin Dowex-1. Encouraged by these results, Hague and co-workers[41] in 1954 made preliminary investigations on the separation of titanium, tungsten, molybdenum, and niobium using various hydrochloric acid - hydrofluoric acid mixtures. The results of many publications by Kraus and co-workers on ion-exchange separations are collected together and discussed in an excellent review by Kraus and Nelson[42] published in 1958. In that review, separations using the hydrochloric acid-hydrofluoric acid system are discussed at length. This system was developed because, in their work with the hydrochloric acid system,[42] they found that species such as zirconium(IV), hafnium(IV), niobium(V), tantalum(V), and protactinium(V) tended to hydrolyze, polymerize, or precipitate even in fairly concentrated hydrochloric acid solutions. In the presence of fluoride this hydrolysis was prevented because of the formation of stable fluoro complexes. The ion exchange behaviors of many elements in hydrochloric acid solution are modified by the addition of hydrofluoric acid. The extent of complexing of various metals by fluoride ion in hydrochloric acid solutions has been calculated by Kraus et al.[43] and such data are shown in Table 3.

The original paper[42] should be consulted for details, but the behavior of a metal on a column of anion-exchange resin can be ascertained from a plot of the logarithm of the distribution coefficient of the metal between the resin and solution against the molarity of hydrochloric acid

TABLE 3

Complexing of Various Metals by Fluoride Ions in Hydrochloric Acid Solutions (Containing 1 M Hydrofluoric Acid)

Element	Fraction of element as fluoride complexes in hydrochloric acid of various molarities						
	0.5	1	2	4	6	8	11
Sn(II)	0.98	0.96	0.9	0.7	0.2	N[a]	→
Fe(III)	←	>0.98	0.98	0.8	0.1	N	→
Ga(III)	←	>0.98	0.98	0.9	0.5	0.3	N
Sb(III)	←	(-)[b]	>0.99	0.7	N	→	→
Ti(IV)	←	←	(-)	←	←	←	>0.97
Zr(IV)	←	←	(-)	←	←	←	>0.999
Hf(IV)	←	←	(-)	←	←	←	>0.999
Ge(IV)	←	←	(-)	←	←	←	>0.994
Sn(IV)	←	←	(-)	0.9	0.5	0.1	N
U(IV)				←	←	>0.99	→
Pa(V)	←	←	(-)	←	←	←	>0.999
Sb(V)	←	←	(-)		0.95	0.9	
Mo(VI)	←	←	(-)	0.9	0.7	0.4	N
W(VI)	←	←	(-)	←	>0.9	0.8	0.6
U(VI)	←	(-)	>0.88	0.4	N	→	→

[a] N means that the fraction of element as fluoride complexes is negligible.

[b] (-) means that there is evidence for the predominance of negatively charged fluoride complexes.

(From Nelson, F., Rush, R. M., and Kraus, K. A., *J. Amer. Chem. Soc.*, 82, 339 (1960). With permission.)

in the presence of a fixed concentration of hydrofluoric acid, such as 1 *M*. Schemes for separating various elements can be devised forwardly from such data, and Kraus et al.[42,43] show a number of examples.

Faris[44] has presented extensive data on the absorption of elements from hydrofluoric acid (1 to 24 M) by Dowex 1-X10 anion-exchange resin. With the exception of niobium(V), the absorbability of every element forming an anionic complex in hydrofluoric acid decreases regularly with increasing molarity of the acid. The following species are strongly absorbed from dilute hydrofluoric acid solutions: beryllium(II), scandium(III), titanium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum(V), molybdenum(VI), tungsten(VI), rhenium(VII), palladium(II), platinum(IV), gold(III), mercury(II), boron(III), tin(IV), arsenic(V), antimony(V), and tellurium(IV). Many of these elements form highly stable anionic fluoro complexes in fluoride media (see Section II A), so it is to be expected that they will be absorbed strongly from dilute hydrofluoric acid solutions. However, it would appear that the hydrochloric acid - hydrofluoric acid system is a better system than the hydrofluoric acid system in that it provides more and better possibilities for column separations of elements for the analytical chemist. Many more useful separations can be achieved with the former system because many elements, in fairly concentrated hydrochloric acid, form stable anionic chloro complexes which are strongly absorbed by anion exchangers.

Cation-exchange separations of metal ions by elution with dilute hydrofluoric acid have been reported by Fritz and co-workers.[45] From Dowex 50W-X8 cation-exchange resin in the hydrogen form the following species are readily eluted with 0.1 *M* hydrofluoric acid: aluminum(III), cadmium(II), molybdenum(VI), niobium(V), scandium(III), tin(IV), tantalum(V), titanium(IV), uranium(VI), tungsten(VI), and zirconium(IV). It will be noted that many of these form stable anionic fluoro complexes and it is not surprising that they are eluted so readily.

Nikitin[46] has also used a cation-exchange resin

column and hydrofluoric acid solutions of different concentrations to separate many inorganic species into groups.

Although these fundamental investigations with solutions of single ions and simple mixtures are most valuable and interesting, the analytical chemist in industry has to analyze "real" materials and is more interested in knowing if ion-exchange methods involving hydrofluoric acid and fluorides can be applied to analyses of complex alloys and other materials. In this direction worthwhile contributions have been made by Wilkins,[47] Hague and Machlin,[48] and Dixon and Headridge.[49,50]

Wilkins[47] has devised a scheme for the separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum in a high-temperature alloy by anion exchange. The flow sheet for the analysis of the alloy is shown in Figure 2. The method was then applied with good results to a sample simulating a high-temperature alloy.

Titanium plus zirconium, niobium, and tantalum have been separated from an anion-exchange resin by elution with mixtures containing ammonium chloride, hydrochloric acid, and hydrofluoric acid in results reported by Hague and Machlin.[48] A preliminary precipitation with cupferron was required to isolate these elements from solutions of steels. The separated elements were determined in the column eluates by well-established gravimetric or photometric procedures. Good results were obtained when the method was applied to steels.

Headridge and Dixon[49] determined the distribution coefficients of many elements likely to be found in complex alloys between hydrochloric acid - hydrofluoric acid solutions and the ion-exchange resins De-Acidite FF® (anionic) and Zeo-Karb 225 (cationic). From a study of the results a scheme was proposed for the separation of these elements into more manageable groups. This was followed by a detailed study of the absorption of titanium, zirconium, niobium, tantalum, molybdenum, and tungsten on De-Acidite FF® from solutions containing mixtures of 2 or more of the compounds hydrofluoric acid, hydrochloric acid, ammonium fluoride, and ammonium chloride, with a view to obtaining a separation scheme for these elements that could be completed within 5 hr.[50] A completely satisfactory separation scheme was achieved, after determining the weight distribution coefficients of these elements between aqueous solutions of the above reagents and the resin, and after investigating numerous elution curves for these elements from columns of the resin.

Titanium(IV), zirconium, niobium(V) tantalum, molybdenum(VI), and tungsten(VI) were retained on the resin and separated from aluminum, vanadium(IV), chromium(III), manganese(II), iron(III), cobalt(II), nickel, and copper(II) by passing a solution of these elements in 1 M hydrofluoric acid through a column of 100 to 200-mesh resin in the chloride form. Titanium plus zirconium, tungsten, niobium, molybdenum, and tantalum were then quantitatively eluted from the resin with 0.01 M hydrofluoric acid - 9 M hydrochloric acid, 3 M hydrofluoric acid - 10 M hydrochloric acid, 0.2 M hydrofluoric acid - 7 M hydrochloric acid, 3 M hydrofluoric acid - 3 M hydrochloric acid, and 1 M ammonium fluoride - 4 M ammonium chloride mixtures, respectively. This separation is shown in Figure 3.

Good results were obtained when the scheme was applied to the separation of these elements in synthetic mixtures and alloys, spectrophotometric or titrimetric[51-53] methods being used for quantitatively determining the separated elements.

The volume distribution coefficients for 19 metals between Dowex 1-X4 resin and nitric acid - hydrofluoric acid mixtures (1 to 12 M in nitric acid, and 0.2 to 5 M in hydrofluoric acid) have been determined by Huff.[54] From these results a method was developed for the quantitative determination of trace elements in tantalum or trace amounts of tantalum in other matrices. Anion-exchange separations involving fluoride solutions have also been employed for the determinations of molybdenum, titanium, and zirconium in tungsten;[55] of niobium and tantalum in stabilized chrome-nickel steel;[56] and of nickel, cobalt, copper, iron, and zinc in molybdenum and tungsten.[57]

The absorptions of many ions arising from complex alloys on an anion-exchange resin from solutions containing hydrofluoric acid (0.1 or 1.0 M) and either nitric or sulfuric acid (0.1 or 1.0 N) have been studied by Danielsson.[58] The absorption behaviors of metal ions in some of these acid mixtures are shown in Table 4.[59] It can be concluded that these systems, which are fairly similar in behavior, are less versatile than the hydrochloric acid - hydrofluoric acid system for achieving separations.

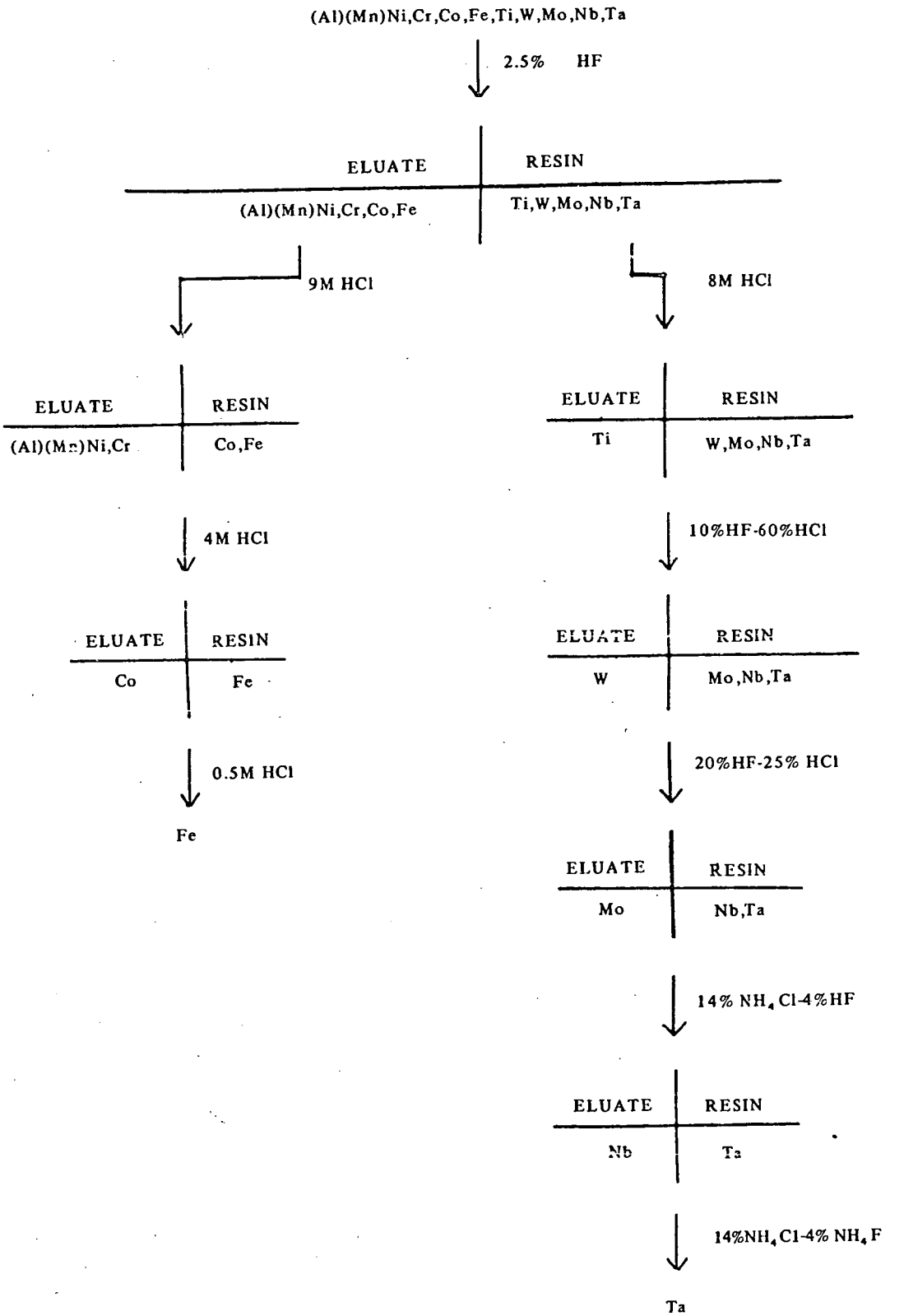

FIGURE 2. Flow sheet for the analysis of a high temperature alloy. (From Wilkins, D. H., *Talanta*, 2, 355 (1959). With permission.)

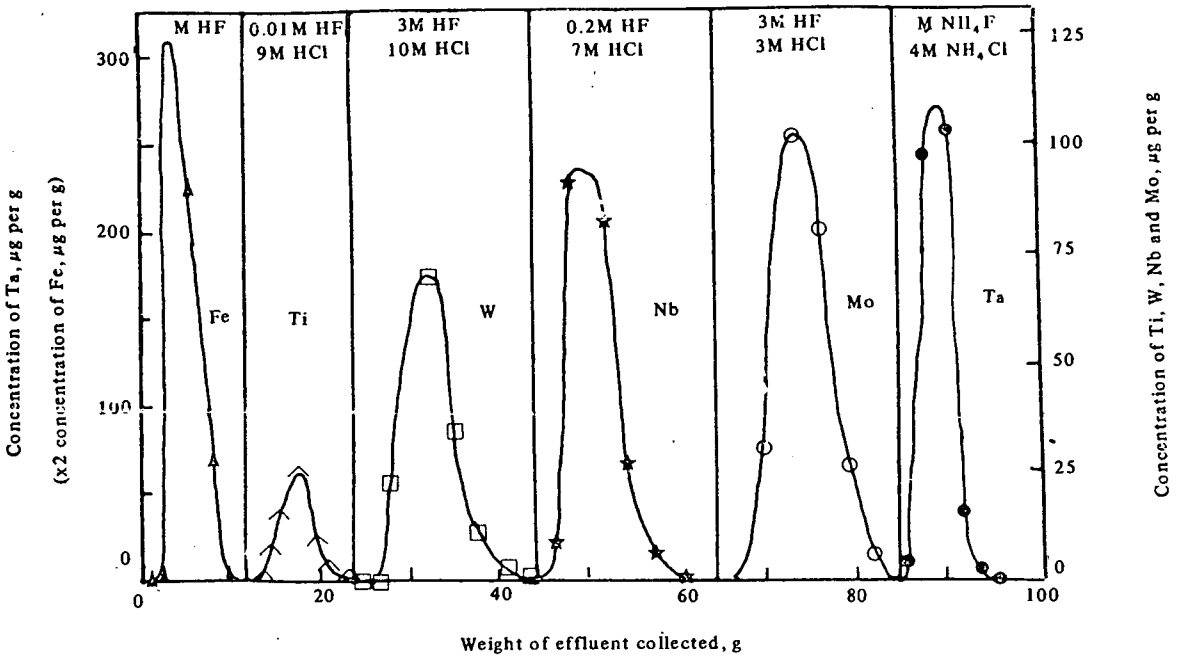

FIGURE 3. Elution curves for the separation of a mixture containing iron, titanium, tungsten, niobium, molybdenum, and tantalum; eluants as shown. (From Headridge, J. B. and Dixon, E. J., *Analyst*, 89, 185, (1965). With permission.)

Danielsson has also investigated the cation-exchange separations of traces of metals from large amounts of iron[60,61] or aluminum,[62] and the anion-exchange separation of traces of metals from large amounts of iron.[63] He summarizes studies on ion-exchange separations, with particular reference to the analysis of iron and steel, in a very useful review.[59]

Further examples of analytical methods involving a preliminary separation on a column of ion-exchange resin using solutions containing hydrofluoric acid are as follows. Lead has been separated from elements, including iron(III), that would interfere with its polarographic determination by absorption on a column of strongly acidic cation-exchange resin in the hydrogen form from 1 M hydrofluoric acid.[64] The lead was eluted with 2 M hydrochloric acid and determined by dc polarography. The method has been applied to the determination of lead in steels.

Niobium has been separated from iron and several other elements by absorption on an anion-exchange resin from a solution containing 1 M hydrofluoric acid and 0.05 M nitric acid. Niobium, held by the resin, was eluted with 4 M nitric acid - 1 M hydrofluoric acid and finally determined photometrically with 4-(2-pyridylazoresorcinol).[65]

Eluants containing hydrofluoric acid have also been used in schemes for the separations of lead, bismuth, and polonium;[66] zirconium, neptunium, and niobium;[67] and uranium, neptunium, and plutonium;[68] while uranium(VI) has been separated from rare-earth elements by elution of uranium(VI) with 1 M ammonium fluoride, sodium fluoride, or hydrofluoric acid from the mixture retained on a cation-exchange resin.[69]

Finally, Ferraro[70] has recently described an ion-exchange method involving eluants containing hydrofluoric acid for the determination of vanadium, zirconium, hafnium, titanium, molybdenum, tungsten, and tantalum in niobium alloys.

B. Separations by Cellulose and Paper Chromatography

Hydrofluoric acid has been incorporated in eluants used for the separation of niobium and tantalum on a column of cellulose. This separation is less convenient than an ion-exchange separation of these elements, but a typical procedure[71] involves the use of a column of activated cellulose in methyl ethyl ketone. A mixture of niobium and tantalum as fluoro complexes on the top of the column is treated by passing methyl ethyl ketone saturated with water down the column. Tantalum

TABLE 4

Approximate Absorption Behaviors of Metal Ions in Solutions Containing 1 M HF and 0.1 *N* H_2SO_4 or HNO_3

	Cation exchange
Weakly absorbed (D<10)[a]	Al(III), As(III), As(V), Cr(III), Fe(III)[b], Mo(VI), Nb(V), Sb(III), Sb(V), Sn(IV), Ta(V), Ti(IV), V(V), W(VI), Zr(IV)
Moderately absorbed (D = 10 to 100)	Bi(III)[b], Fe(II)[b], V(IV)[b]
Strongly absorbed (D>100)	Ag(I), Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II), Zn(II)
	Anion exchange
Weakly absorbed (D<10)	Ag(I), Al(III), As(III), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II), Sb(III), V(IV), Zn(II)
Moderately absorbed (D = 10 to 100)	As(V), V(V)
Strongly absorbed (D>100)	Mo(VI), Nb(V), Sb(V), Sn(IV), Ta(V), Ti(IV), W(VI), Zr(IV)

[a] D is the weight distribution coefficient.

[b] If the concentration of HF is decreased to 0.1 M these elements are strongly absorbed.

(From Danielsson, L., *Ark. Kemi*, 27, 467 (1967). With permission.)

is eluted, and niobium is then stripped from the column with methyl ethyl ketone containing 7.5% (v/v) of concentrated hydrofluoric acid.

Niobium and tantalum can be separated satisfactorily by paper chromatography using hydrofluoric acid and methyl isobutyl ketone,[72] and niobium, tantalum, and titanium have been separated on Whatman No. 1 paper using diethyl ketone saturated with 2.2 M hydrofluoric acid - 2 M nitric acid. The R_f-values are 0.05 for titanium, 0.55 for niobium, and 1.00 for tantalum.[73] The paper chromatographic behaviors of many inorganic substances with solvents containing hydrofluoric and hydrochloric acids have also been reported by Popa and co-workers.[74]

V. SOLVENT EXTRACTION

A. Basic Considerations

In the presence of excess hydrofluoric acid or fluoride, there are many elements that form stable anionic fluoro complexes. These anions may be extracted into organic solvents as ion-association complexes, in which the cation may be either the protonated solvent or some other bulky ion, such as a tetraalkylammonium ion. In actual fact, satisfactory extraction methods have only been devised for boron and tantalum, and to a much more limited extent for niobium and protactinium.

Early studies were made by Kitahara[75] and

TABLE 5

The Extent of Extraction of Elements into Diethyl Ether from 20 M Hydrofluoric Acid Solution

Percentage extracted	Elements in each class
< 1	Al, Ca, In, Tl(I), Si, Sb(V), Ti(IV), Cr(III), W(VI), Fe(II), Fe(III), Ni, Ag, Zn
1 to 10	Be, Ge(IV), Sn(II), Sn(IV), Sb(III), Zr(IV), V(V), Mo(VI), Mn(II), Co(II), Cu(II), Cd, Hg(II), U(VI)
10 to 50	P(V), As(III), As(V), Se(IV), Te(IV), V(III)
> 50	Nb(V), Ta(V), Re(VII)

Bock and Herrmann[76] on the solvent extraction of many elements into diethyl ether from hydrofluoric acid solutions. The extent of extraction increases with the concentration of hydrofluoric acid in the aqueous phase. Data on the extractions of many elements from 20 M hydrofluoric acid are presented in Table 5.[76]

From aqueous solutions containing 10 to 20 M hydrofluoric acid, this acid is extracted to the extent of approximately 38%.[76] Work on the solvent extraction of elements from fluoride solutions up to 1956 has been ably reviewed by Morrison and Freiser.[77]

It will be noted from Table 5 that niobium and tantalum are appreciably extracted into diethyl ether from 20 M hydrofluoric acid. Niobium(V) is nearly quantitatively extracted from 6 M hydrofluoric acid - 6 M sulfuric acid into diisobutylcarbinol[78] and from 10 M hydrofluoric acid - 6 M sulfuric acid - 2.2 M ammonium fluoride into methyl isobutyl ketone.[79] With this latter system the extraction of tantalum is also almost complete. This solvent-extraction procedure has been used in a method to determine niobium in titanium ores and pigments.[80]

Niobium and tantalum can be separated fairly effectively by extracting the tantalum into diisopropyl ketone from an aqueous solution 0.4 M in hydrofluoric acid and approximately 4 M in hydrochloric, nitric, sulfuric, or perchloric acid.[81] A double extraction procedure for the separation of tantalum from niobium, using a hydrochloric-hydrofluoric acid medium and methyl isobutyl ketone, has been devised by Theodore,[82] and a colorimetric determination of tantalum in niobium has been reported after separation of the tantalum by extraction into cyciohexanone from 0.4 M hydrofluoric acid - 2 M sulfuric acid solution.[83] Protactinium(V) is almost completely extracted into diisopropyl ketone from 8 M hydrochloric acid - 0.6 M hydrofluoric acid - saturated aluminum chloride.[84]

Maeck and co-workers[85] have investigated the distributions of 57 metallic ions between methyl isobutyl ketone and an aqueous phase containing 0.2 to 5 M hydrofluoric acid and tetrapropyl-, tetrabutyl-, or tetrahexylammonium ions. Distribution data are presented as plots of percent extraction versus molarity of hydrofluoric acid in the form of a periodic table. These plots show that, for these metals, the only important extractable fluoride complex is that of tantalum(V). Niobium(V) and protactinium(V) are scarcely extracted, but high percentages of technetium(VII) and rhenium(VII) are extracted. Tantalum is also extracted from 0.15 M hydrofluoric acid - 8 M hydrochloric acid using 10% (v/v) Amberlite LA-2® in benzene[86] and can be separated from niobium, titanium, and zirconium by solvent extraction of tetraphenylarsonium fluotantalate into dichloroethane or chloroform.[87]

Using a 3% (w/v) solution of triisooctylamine in carbon tetrachloride and an aqueous solution containing niobium(V) and tantalum(V) together with 1.33 M nitric acid and 0.24 M hydrofluoric acid, Marchart and Hecht[88] have shown that 98%

of the tantalum is extracted into the organic phase on shaking while 98% of the niobium remains in the aqueous phase. From 0.5 to 2 M hydrofluoric acid, with or without sulfuric acid, tantalum is extracted to the extent of 90 to 95% with 1 volume of tributylphosphate, while only 2.5 to 5% of the niobium is extracted.[89] From solutions 6 M in hydrofluoric acid and 8 M in sulfuric acid, 1 volume of tributylphosphate extracts 100% of the tantalum and 97.5 to 99.5% of the niobium. From 1 M hydrofluoric acid, tantalum is also extracted and may be separated from niobium by shaking with an equal volume of a solution consisting of tri-n-butylphosphate-kerosene (4:1,v/v).[90]

It would appear that tantalum is readily extracted from mildly acidic fluoride solutions, but that niobium is best extracted from strongly acidic solutions containing high concentrations of hydrofluoric acid. With the latter systems tantalum will usually be extracted also.

Another element that can be extracted as a fluoro complex is boron. At a pH less than 3.2 in the presence of fluoride and tetraphenylarsonium chloride, this element is extracted into chloroform as the tetraphenylarsonium tetrafluoborate ion-association complex.[91]

B. Solvent Extraction Followed by Spectrophotometric Determination

It has been seen that boron and tantalum are readily extracted as ion-association complexes from fluoride solutions into organic solvents. If the cationic part of an ion-association complex is a dyestuff such as methyl violet, then the extracted complex will be colored, providing the basis for a colorimetric determination of the extracted element.

1. Determination of Boron

Methods for the determination of boron are summarized in Table 6. There seems to be little

TABLE 6

Methods for the Solvent Extraction and Spectrophotometric Determination of Boron

Cationic Reagent	Solvent	Comments	Ref.
Methylene blue	1,2-Dichloroethane	In water, Si, and SiO_2; no interference from Al, Fe(III), and Si	92
		In steel	93,94,95 96,97,98
		In Al and its alloys	99
		In Zr and Zircaloy	100
		In rocks	101
Monomethylthionine (Azure C)	1,2-Dichloroethane	Preferred to methylene blue	102
Methyl violet	Benzene	pH 3.4	103,104
	Trichloroethylene	In steel	105
Brilliant green	Benzene	In steel	106
		In Ti and Zr metals	107
Crystal violet	Benzene	–	108
Malachite green	Benzene	Cl^-, I^- and NO_2^- interfere	109
Brilliant Cresyl Blue Capri Blue Nile Blue	1,2-Dichloroethane	–	110
Nile Blue A	Chlorobenzene or *o*-dichlorobenzene	In fertilizers, soil, plants, and water	111
Tris(1,10-phenanthroline) iron(II)	*n*-Butyronitrile	Measure at 520 nm	112
	Nitrobenzene	Alkylbenzenesulfonates and SCN^- interfere	113
Methyl green	Trichloroethylene	pH 2.5 to 5.0	114
Rhodamine B	Butyl acetate	Measure at 555 nm	115

ground for choice among these reagents for the spectrophotometric determination of boron.

2. Determination of Tantalum

Methods for the determination of tantalum are summarized in Table 7. The optimum pH-values for the extraction of fluotantalate from aqueous solution into benzene as ion-association complexes are 1.9 to 2.2 with methyl violet, 1.6 to 2.3 with crystal violet, 0.8 to 2.0 with malachite green and 0.6 to 2.0 with brilliant green.[122] Such triphenylmethane dyes form ion-association complexes with tantalum in the form of hexafluotantalate(V).[123] Again it would appear that any of the dyes in Table 7 and of those just mentioned can be satisfactorily used in a spectrophotometric method for tantalum.

In a highly sensitive method reported for the determination of tantalum in silicon dioxide and trichlorosilane, the tantalum is extracted from hydrofluoric acid solution into benzene, using rhodamine 6G, and the concentration of the complex is determined fluorometrically. Parts per hundred million of tantalum can be determined.[124]

3. Determination of Niobium

Butyl rhodamine B has been employed for the extraction into benzene of niobium from 5 M sulfuric acid containing hydrofluoric acid. A subsequent spectrophotometric determination of niobium could then be made. Conditions have been established for the determination of niobium in the presence of tantalum.[125]

C. Solvent Extraction Followed by Flame Photometry

Boron as tetrafluoborate has been extracted into methyl isobutyl ketone as an ion-association complex with tetrabutyl-ammonium ion and subsequently determined by flame photometry.[126] Niobium has been extracted from 6 M hydrofluoric acid - 6 M hydrochloric acid into methyl isobutyl ketone and determined in the organic phase by flame photometry. Tantalum is extracted along with niobium.[127] The method has been applied to the determination of niobium in steels. Finally, niobium and tantalum have been extracted into methyl isobutyl ketone from solutions of nickel-base[5] and cobalt-base[6] alloys in 10 M hydrofluoric acid - 6 M hydrochloric acid before determination by atomic absorption spectroscopy.

TABLE 7

Methods for the Solvent Extraction and Spectrophotometric Determination of Tantalum

Cationic Reagent	Solvent	Comments	Ref.
Methyl violet	Benzene	pH 2.3	103
	Toluene	pH 1.9 to 2.3; in Nb metal; no interference from Ti and Zr	116
Malachite green	Benzene	In Fe, steel, and Nb containing 0.005 to 0.5% Ta*;	8
		in B, U, Zr and U-Zircaloy-2; Ta is first coprecipitated with Fe(III) from aqueous ammoniacal solution	117
Butylrhodamine B Rhodamine 6G	Benzene		118
Nile Blue A	Chlorobenzene	In steel and Nb	119
Victoria Blue B	Benzene	2 *M* H_2SO_4 to 0.5 *M* HF	120
Meldola Blue	Chlorobenzene	In Nb metal	121
Methyl Green	Benzene	pH 0.8 to 1.7	114

*Boron, which forms a similar complex, is removed by fuming with sulfuric acid in the presence of hydrofluoric acid to volatilize it as boron trifluoride.

VI. PRECIPITATION FROM FLUORIDE–CONTAINING MEDIA

Many elements form insoluble or sparingly soluble fluorides. These include lithium, magnesium, calcium, strontium, barium, lead, scandium, yttrium, and lanthanides and actinides in the +3 and +4 oxidation states. This fact has been used to develop separation methods for certain groups of elements. However, little use has been made of fluoride precipitates in direct gravimetric analysis, probably because fluoride precipitates are often gelatinous and difficult to filter. Precipitation from homogeneous solution should yield more compact precipitates. Most of the basic facts on insoluble fluorides were discovered before 1960 and few papers appear to have been published on the precipitation of fluorides in the last decade. The decreasing interest in gravimetric analysis as a field for research in recent years probably contributes to this fact.

It is stated that lithium can be determined gravimetrically as the fluoride,[128] but the method offers no advantages over better-established methods such as precipitation as a complex periodate.[129] Calcium has been determined by precipitation as calcium fluoride from homogeneous solution. The fluoride ion was produced by the hydrolysis of tetrafluoborate ion in the presence of ammonium chloride and urea at 95° C. Magnesium and lead interfere.[130] Apparently lead can also be determined gravimetrically as lead chlorofluoride.[131]

Scandium forms an insoluble fluoride and in dilute aqueous hydrofluoric acid solution can thus be separated from titanium, niobium, and tantalum.[132] However, care must be taken to see that the concentration of excess of fluoride is kept low because scandium trifluoride readily forms a soluble anionic fluoro complex in solutions containing high concentrations of fluoride. Indeed, this reaction has been used by Meyer and coworkers[133] to separate scandium fairly effectively from thorium. Its use has been further evaluated by Fischer and Bock.[134]

Rare earths are separated from niobium, tantalum, titanium, zirconium, and iron by precipitation as insoluble fluorides on addition of hydrofluoric acid. The other elements are held in solution as soluble fluoro complexes provided that the alkali metal ions, which form insoluble complex fluorides with these elements, are absent or present at only low concentration.[135] Thorium and uranium(IV) are precipitated as insoluble fluorides along with the rare earths, but calcium and lead are precipitated incompletely. Care must be taken to keep the concentration of excess fluoride fairly low, for there is a tendency to form soluble complex rare earth fluorides in media containing high concentrations of fluoride. The gravimetric determination of rare earths by collecting and weighing their precipitated fluorides does not appear to have been reported. Rare earth fluoride precipitates are usually dissolved by treatment with sulfuric acid or with a mixture of nitric and perchloric acids and the solution subjected to further analysis. Lanthanum fluoride has been produced by precipitation from homogeneous solution by boiling a nitric acid solution containing fluoboric acid and urea.[136] A good account of the precipitation of rare earth fluorides, with many references, is given by Ryabchikov and Ryabukhin.[137]

Thorium is precipitated as hydrated thorium tetrafluoride by the addition of hydrofluoric acid to soluble thorium salts at room temperature. At 300° C the anhydrous tetrafluoride is formed, but this is not a suitable weighing form because partial hydrolysis occurs on heating in the atmosphere. Small amounts of thorium fluoride are converted into thorium oxide when ignited at 1,000°C.[138] Yttrium and lanthanum fluorides are good carriers for the precipitation of trace amounts of thorium. Further details on the precipitation of thorium by hydrofluoric acid and alkali fluorides are reported by Ryabchikov and Gol'braikh.[138] Like thorium tetrafluoride, uranium(IV) fluoride is insoluble in aqueous hydrofluoric acid solutions, and this permits the separation of uranium(IV) from uranium(VI). The compound $UF_4 \cdot NH_4F \cdot 0.5H_2O$ may also be used for the quantitative separation of uranium(IV) from uranium(VI), iron(III), and vanadium(III).[139] An extensive account of the precipitation of uranium(IV) fluoride in the presence of other elements such as zirconium and tantalum is given by Palei.[140]

Neptunium, plutonium, and americium in the +3 and +4 oxidation states can be precipitated from solution as fluorides using lanthanum fluoride as a carrier. Insoluble fluorides of the rare earths and thorium accompany these actinides.[141] The transamericium elements in their +3 oxidation state are also coprecipitated along with rare earths by fluoride and thereby collected.[142] The in-

soluble double salt $NaPuF_5$ is formed when an excess of sodium fluoride is added to a nitric acid solution of plutonium(IV).[143] By using this reaction, plutonium could be separated from those elements such as iron(III) and titanium, which are present as soluble species under these conditions.

VII. TITRIMETRIC ANALYSIS

A. Redox Titrations

1. General Considerations

From a study of the data on stability constants in Section IIA, it is evident that, compared with most singly and doubly charged cations, the cations of higher charge form more stable complexes with fluoride ion. This is reflected in an appreciable lowering of the values of the formal potentials of M(III)/M(II) couples in fluoride media compared to the values in noncomplexing media. Some couples which one would expect to be affected are vanadium(III)/vanadium(II), chromium(III)/chromium(II), manganese(III)/manganese(II), iron(III)/iron(II), and cobalt(III)/cobalt(II). The measured values for certain formal potentials in 0.5 M ammonium fluoride - 0.5 M hydrofluoric acid are shown in Table 8 along with the corresponding formal potentials for the uncomplexed ions.[144]

By combining the estimated overall stability constants (β_6) of the hexafluomanganate(III) and hexafluoferrate(III) anions with the Nernst equation, Headridge and Taylor[145] calculated that the formal potentials of the manganese(III)/manganese(II), iron(III)/iron(II), and manganese(VII)/manganese(III) couples should be +0.86 V, +0.06 V, and +1.29 V, respectively, assuming that manganese(II), iron(II), and permanganate were not complexed by fluoride. These calculated results are in fairly good agreement with the experimental results reported in Table 8. Clearly, iron(II) in certain fluoride media is a powerful reducing agent. The formal potentials indicate that it should be possible to oxidize manganese(II) to manganese(III) with potassium permanganate in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid. The results that have been obtained with these systems will be described later. One would also expect chromium(II) and vanadium(II) in suitable fluoride media to be very powerful reducing agents, which would probably react rapidly with hydrogen ion to reduce it to molecular hydrogen. Cobalt(III) should be appreciably stabilized by complex formation with fluoride and it may be possible to devise an analytical method for the titrimetric oxidation of cobalt(II) to cobalt(III) in the presence of fluoride. The applications of some of these couples in titrimetric analysis are described below.

2. The Manganese(VII)/Manganese(III) System

As illustrated in Table 8 at pH-values around 3 permanganate becomes a more powerful oxidant in the presence of free fluoride ions than in their absence. However, it must be appreciated that the hydrogen-ion concentration has a pronounced effect on the formal potential of the manganese(VII)/manganese(III) couple.

$$MnO_4^- + 8H^+ + 6F^- + 4e \rightleftharpoons MnF_6^{3-} + 4H_2O.$$

TABLE 8

Formal Potentials in 0.5 M Ammonium Fluoride – 0.5 M Hydrofluoric Acid and in a Noncomplexing Medium

System	$E^{O'}$(fluoride medium) (V vs. N.H.E. at 25° C)	$E^{O'}$(uncomplexed ions)* (V vs. N.H.E. at 25° C)
Mn(III)/Mn(II)	+0.87	+1.51
Fe(III)/Fe(II)	+0.10	+0.77
Sn(IV)/Sn(II)	+0.05	+0.15
Mn(VII)/Mn(III)	+1.30	+1.13
Cr(VI)/Cr(III)	+0.95	+0.92
V(V)/V(IV)	+0.71	+0.62

*These values are calculated, where applicable, for the pH (3.15) of 0.5 *M* ammonium fluoride - 0.5 *M* hydrofluoric acid.

As the hydrogen-ion concentration is increased, the fluoride-ion concentration is decreased due to the formation of undissociated hydrofluoric acid. In strongly acidic solutions the addition of fluoride ion will have no pronounced effect on the formal potential of the manganese(VII)/manganese(III) couple.

Potentiometric end-point detection has been employed by Issa and Hamdy[146] in the titration of mercury(I) with permanganate in sulfuric acid solution in the presence of fluoride. The permanganate is reduced to manganese(III). A visual titration of mercury(I) is possible in the presence of copper sulfate, which is added to mask the color of the manganese(III) ion. The method has also been applied to the determination of tellurium(IV) in acidic fluoride solution by titration with standard permanganate solution,[147] after the addition of mercury(I), which presumably serves as a catalyst. Selenium(IV) in sulfuric acid solutions containing fluoride has been determined by adding excess potassium permanganate, waiting 30 min, and back-titrating the excess with mercurous nitrate solution.[148] It seems likely that mercury(I), selenium(IV), and tellurium(IV) could be determined equally well in the absence of fluoride.

Issa and Hamdy have also determined iron(II)[149] and chromium(III) and vanadium(IV),[150] by adding excess potassium permanganate in sodium hydroxide solution, allowing the solution to stand for 5 min, acidifying with sulfuric acid, adding sodium fluoride solution and then an excess of standard mercury(I) solution, and back-titrating the excess with permanganate in the presence of copper sulfate

An interesting titration is that of manganese(II) with permanganate in the presence of fluoride. Zvenigorodskaya and Gotsdiner[151] performed this titration, employing potentiometric end-point detection; manganese(III) is both the product of oxidation of the manganese(II) and the product of reduction of the permanganate, so that the overall reaction is

$$MnO_4^- + 4Mn^{++} + 8H^+ + 30F^- = 5MnF_6^{3-} + 4H_2O$$

Visual determination of the end-point was also possible.[152] These titrations were used for the determination of manganese in ores and slags.

Headridge and Taylor[153] later investigated the accuracy and precision of the titrimetric determination of manganese(II) in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid with 0.02 M permanganate as the titrant. In the absence of colored ions, they found that 2.5 to 15 mg of manganese(II) in 100 ml of solution could be determined by visual titration with a mean error of 0.001 mg and a standard deviation from the mean of 0.020 mg. The manganese(III) fluoride complex anion is pale yellow-brown in color, but after a little practice the merest excess of permanganate can be readily detected by eye even if the titrand contains as much as, or even more than, 15 mg of manganese(II) per 100 ml.

Except for obvious reducing agents, it was considered that only cobalt(II), nickel(II), copper(II), and chromium(III) in fluoride solutions could possibly be oxidized to higher oxidation states by permanganate, but it was soon established that these species were not in fact, oxidized by permanganate, either in the presence or in the absence of manganese(II). The reaction, therefore, seems to be highly selective for manganese(II) in the presence of other elements.

Of course it is much more difficult to obtain accurate results when manganese(II) is titrated visually with permanganate in the presence of colored ions, and in these instances a photometric titration was preferred. A potentiometric titration should be equally satisfactory. Using this method, good results were obtained for the analysis of steels and other alloys containing manganese.

3. The Iron(III)/Iron(II) System

Mahr and Seeger[154] have determined copper(II) by adding excess potassium iodide in the presence of acetate buffer and potassium fluoride, and titrating the liberated iodine with standard ferrous sulfate solution. In the presence of fluoride ion, iron(II) becomes a powerful reducing agent. Variamine Blue, a redox indicator, was used. Alternatively a potentiometric end-point may be employed. The method was applied to the determination of copper in brass and bronze samples. However, it would appear that in the presence of fluoride iron(II) has no advantages over thiosulfate as a titrant for iodine.

From Table 8 it can be seen that iron(II) is a powerful reducing agent in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid. In fact, it is a more powerful reducing agent than tin(II) in 1 M hydrochloric acid ($E^{o\prime}$ = +0.14 V vs. N.H.E.). In 50% (v/v) aqueous alcohol containing 0.5 M ammonium fluoride and 0.5 M hydrofluoric acid, the formal potential of the iron(III)/iron(II)

couple is even less positive, -0.02 V vs. N.H.E., and in this medium the purities of many quinones were determined by Headridge and Wilson[155] by potentiometric titrations with standard iron(II) solution. Any quinone, that forms part of a couple whose formal potential in the aqueous alcoholic mixed fluoride solution is not less than +0.24 V vs. N.H.E. can be determined. These include almost all of the 1,4- and 1,2-benzoquinones and phenanthraquinones, as well as many naphthaquinones, but only a few anthraquinones.

4. Metal Reductors and Fluoride Solutions

In addition to the titrations so far considered, where the fluoride ion has had a pronounced effect on the oxidizing or reducing ability of the titrant or titrand, there are other titration systems where the presence of fluoride ion is desirable. These involve solutions that contain partially hydrolyzed species in the absence of fluoride. In Section IIB, a brief account was given of the beneficial effect of fluoride in inhibiting hydrolysis. The presence of hydrofluoric acid is particularly advantageous in achieving quantitative reduction of niobium(V) and tungsten(VI) with metal reductors before titrimetric determinations of the reduced species with a suitable oxidant as titrant.

Although the titrimetric determination of niobium had been studied by many workers since 1885, no completely satisfactory procedure was reported before the work of Headridge and Taylor[51] published in 1962. Methods for this determination are based on the titration of a solution of niobium after treatment with a metallic reducing agent to convert the element into the tervalent state. The earlier methods reviewed by Schoeller and Waterhouse[156] all yielded low results, probably because of the presence of colloidal niobic acid resulting from hydrolysis. A more satisfactory titrimetric method, proposed and used by Cunningham,[157] was studied in detail by Knowles and Lundell.[158] These workers examined the reduction of niobium(V) in sulfuric acid media and used succinic acid and hydrogen peroxide as complexing agents; their results indicated that reduction was almost complete, but lacked precision. As the most stable complex of niobium in aqueous media is probably the fluoro complex, Headridge and Taylor[51] examined the titrimetric determination of niobium in solutions containing fluoride. Niobium(V) in 6 M hydrochloric acid – 0.5 M hydrofluoric acid was reduced quantitatively in a Jones reductor to niobium(III). The niobium(III) solution was collected in ferric ammonium sulfate solution under oxygen-free nitrogen. An amount of iron(II) was produced equivalent to the amount of niobium(III) present. The iron(II) was determined by titration with 0.0167 M potassium dichromate, using barium diphenylaminesulfonate as indicator. It is essential to the success of this method that the volume of the delivery tube between the column of amalgamated zinc shot and the iron(III) solution be kept to a minimum, for the niobium(III) species is fairly rapidly oxidized by hydrogen ion and the residence time of the niobium(III) solution in the delivery tube should be no more than a few seconds. When this precaution is observed, quantitative reduction of niobium(V) is readily achieved either in the presence or in the absence of tantalum(V), which is not reduced under these conditions. The precision of the method is good.

Before 1950, attempts to determine tungsten by titration of tungsten(III), produced by reduction of tungsten(VI) with metals, were unsuccessful[159] because reduction was not quantitative. Some time later, Geyer and Henze[160] and Luke[161] showed that almost complete reduction can be achieved if strong hydrochloric acid solutions of tungsten(VI) are reduced. Headridge and Taylor[52] found that tungsten(VI) in 2 M hydrochloric acid – 0.5 M hydrofluoric acid can be reduced completely to tungsten(III) using a Jones reductor; the reduced species being collected in ferric ammonium sulfate solution under a nitrogen atmosphere. Thus, the iron(II) produced was titrated with standard dichromate solution as with niobium. Molybdenum(VI), is also reduced to molybdenum(III) under these conditions and, as expected, iron(III) is reduced to iron(II). To ensure that premature oxidation of tungsten(III) by hydrogen ion does not occur, it is again essential to employ a delivery tube of the smallest possible volume. In fact, tungsten(III) reacts with hydrogen ion even more readily than does niobium(III)[52] Neither molybdenum(VI) nor tungsten(VI) in 2 M hydrochloric acid – 0.5 M hydrofluoric acid is at all reduced on a silver reductor at 10°C, although iron(III) is quantitatively reduced to iron(II) under these conditions.[53]

On a silver reductor at 60° C in 0.2 M hydrofluoric acid – 1.5 to 2.0 M hydrochloric

acid, molybdenum(VI) is reduced quantitatively to molybdenum(V); in 0.2 M hydrofluoric acid containing more than 4 M hydrochloric acid, it is reduced quantitatively to molybdenum(III). No reduction of tungsten(VI) in 0.2 M hydrofluoric acid – hydrochloric acid occurs on a hot silver reductor at a hydrochloric acid concentration below 5.5 M.

Solutions containing iron(III), molybdenum(VI), and tungsten(VI) but no other species capable of reduction can, therefore, be analyzed for all three metals by using the Jones and silver reductors. These methods have been applied to the analyses of ferromolybdenum and ferrotungsten.[53]

The behaviors of a few elements that can be quantitatively reduced to lower oxidation states on metal reductors in solutions free from fluoride, were investigated for the fluoride systems employed for iron, molybdenum, and tungsten.[53] The procedures used for the reductions and titrations were identical with those employed for iron, molybdenum, and tungsten. The results are shown in Table 9. As a summary, the results obtained for iron, molybdenum, and tungsten are also included in this table.

TABLE 9

Oxidation States of Titanium, Vanadium, Chromium, Molybdenum, Tungsten, and Iron after Passage through Various Reductors

Species	Oxidation states in the effluent from the reductor		
	Cold silver[a]	Hot silver[b]	Jones[c]
Titanium(IV)	+4.00	+4.00	+3.00
Vanadium(V)	+4.00	+4.00	+2.00
Chromium(III)	+3.00	+3.00	+2.83*
Molybdenum(VI)	+6.00	+3.00	+3.00
Tungsten(VI)	+6.00	+6.00	+3.00
Iron(III)	+2.00	+2.00	+2.00

[a]Using 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid at 10°C.
[b]Using 4.5 *M* hydrochloric acid - 0.2 *M* hydrofluoric acid at 60°C.
[c]Using 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid at 12°C.
*Chromium(III) is not reduced to a definite oxidation state on the Jones reductor in cold 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid.

B. Precipitation Titrations

Calcium in an ethanolic solution of pH 2.5 to 3.5 may be determined by titration with standard sodium fluoride solution using ferric thiocyanate as indicator. The red color of the indicator disappears at the end-point as excess fluoride complexes the iron(III).[162] Likewise, lead in the presence of excess sodium or potassium chloride can be determined by titration with standard sodium or potassium fluoride solution. Insoluble lead chlorofluoride is produced. The end-point is determined potentiometrically when the solution contains low concentrations of both ferrous and ferric ions. A sharp drop in the potential of the indicating electrode occurs at the end-point as the ferric ions are complexed by fluoride.[163]

Using standard sodium fluoride as titrant, thorium may be titrated in the presence of SPADNS as indicator at pH 3. Zirconium, hafnium, molybdenum, and phosphate interfere.[164] Thorium has also been determined by titration in a 50% (v/v) alcoholic solution at pH 2 with standard sodium fluoride solution using Alizarin Red S plus Pyrocatechol Violet as indicator. Thorium may be determined in monazite using this method.[165]

These titrations with sodium fluoride solution are interesting, but determinations of these elements by complexometric titrations with EDTA are much more popular.

VIII. POLAROGRAPHY AND VOLTAMMETRY IN FLUORIDE MEDIA

A. Polarography

The analytical chemist is likely to use the simplest system consistent with his requirements and, therefore, in polarography he is unlikely to use base electrolytes containing fluoride if simpler base electrolytes can be employed. However, we have already seen that the fluoride ion, being a good complexing agent, has a pronounced effect on the formal potentials of certain couples. The use of fluoride in polarography is, therefore, advantageous if it produces separate waves for two species whose waves are superimposed in non-complexing supporting electrolytes. With these objects in mind, detailed polarographic investigations have been undertaken by West and co-workers[166] and by Headridge and co-workers.[167,168] Data from these papers and a few

others are presented in Table 10. The results for the similar supporting electrolytes 1 M ammonium fluoride[168] and 1 M sodium fluoride[166] are in reasonable agreement.

For polarography in 0.1 M hydrofluoric acid – 0.1 M ammonium fluoride, Headridge et al.[167] used a Teflon® dropping mercury electrode identical with the one described by Raaen.[172] Glass capillaries are not suitable for use as dropping mercury electrodes at pH < 4, for they are then attacked by hydrofluoric acid. If lead is to be determined in supporting electrolytes containing fluoride, Pyrex® rather than lead-glass capillaries should be used.

It can be seen from Table 10 that species strongly complexed by fluoride are indeed reduced at much more negative potentials in fluoride media than in noncomplexing media. The strong fluoride complexes are also often reduced very irreversibly. Well-formed waves with half-wave potentials less negative than -1.0 V vs. S.C.E. are, however, obtained for bismuth(III), cadmium(II), lead(II), antimony(III), and thallium(I) in these fluoride media, and the polarographic determination of, for example, bismuth in titanium-, zirconium-, niobium-, tantalum-, or tungsten-base material in acidic or neutral fluoride solutions should be straightforward. Hamza and Headridge[168] did, in fact, determine lead in a nickel-titanium alloy using 1 M ammonium fluoride at pH 7 as a supporting electrolyte. For the determination of trace amounts of such elements a differential cathode-ray or pulse polarograph should be employed.

Verbeek and co-workers[173] have shown that reduction waves due to ferric iron are not present up to a concentration of 0.05 M in neutral 0.75 M sodium fluoride provided that the pH of the iron solution is between 2 and 3 before addition of the fluoride. Presumably different iron(III)-fluoride complexes are formed when this procedure is adopted and when an iron(III) salt is dissolved in the base electrolyte directly, because when using the latter procedure with 1 M ammonium fluoride, Hamza and Headridge[168] obtained 2 reduction waves for iron(III). Using the former procedure, Verbeek et al.[173] were able to determine uranium(VI) polarographically in the presence of up to 400-fold excess of iron(III).

Headridge and Hubbard[174] also used polarography in 0.5 M hydrofluoric acid – 0.5 M sulfuric acid for the determination of molybdenum (about 5%) in niobium-base alloys that also contained 15% tungsten. In this supporting electrolyte, molybdenum(VI) produces two waves with half-wave potentials of -0.06 V ($E_{1/4} - E_{3/4}$ = 100 mV) and -0.52 V vs. S.C.E. ($E_{1/4} - E_{3/4}$ = 140 mV). The first wave results from the reduction of molybdenum(VI) to molybdenum(V) and the second from the reduction of molybdenum(V) to molybdenum(III). For the analysis of the niobium-base alloys a polyethylene cell with a mercury-pool anode was used, and diffusion current measurements were made on the first wave at a potential 0.15 V more negative than the half-wave potential. The results obtained by this polarographic method and a thiocyanate spectrophotometric method were in good agreement.

B. Voltammetry

Using a rotating platinum electrode, Hamza and Headridge[175] have also investigated the voltammetric behaviors of 19 ions in 1 M ammonium fluoride. The voltammetric data are shown in Table 11.

The oxidation wave for manganese(II) to manganese(IV) is particularly interesting and has been used successfully to determine manganese in steels and cast iron of low cobalt content. Any interference from vanadium(IV) was obviated by oxidizing it to vanadium(V) with a slight excess of dichromate, which has no effect upon manganese(II).

IX. MISCELLANEOUS

A. Fluoride as a Masking Agent

Because fluoride forms stable complexes with the ions of such elements as beryllium, aluminum, silicon, germanium, tin, titanium, zirconium, hafnium, niobium, and tantalum, the reactions of these ions with many other analytical reagents can be prevented by the addition of fluoride ions. Species that are not strongly complexed by fluoride are able to react with the other analytical reagents in a more selective way. Fluoride is frequently used as a masking agent, but only a few examples will be given to illustrate this point.

Precipitation of tin(IV) as sulfide is prevented in the presence of fluoride ion, which forms a very stable fluoro complex with tin(IV). This serves as a means of separating lead and copper as insoluble sulfides from tin(IV)

TABLE 10

Polarographic Data for Inorganic Species in Fluoride Solutions

Species	Supporting Electrolyte					
	0.1 *M* HF - 0.1 *M* NH_4F (Ref. 167)		1M NH_4F (pH 7) (Ref. 168)		1M NaF (Ref. 166)	Others
	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/4} - E_{3/4}$ (mV)	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/4} - E_{3/4}$ (mV)	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/2}$ (V vs. S.C.E.)
Ag(I)	Reduced chemically by Hg		> 0		> 0	
As(III)	−0.84; −0.88	waves cover 0.6 V	about −1.40[m]	very irreversible		
As(V)	> 0; −0.8	second wave small and very irreversible	N.R.[a]			
Bi(III)	−0.13	19	−0.27	35	−0.07 (pH 0.7 to 2.1)	
Cd(II)	−0.59	30	−0.61	27	−0.63 (pH 3.1 to 6.7)	
Co(II)	I.S.H.W.*		−1.32	110	−1.38 (pH 2.9 to 6.0)	
Cu(II)	+0.08; −0.07	waves cover 0.3 V	+0.02; −0.16	waves cover 0.35 V	0.00 (pH 5.1)	
Fe(II)	N.R.		about −0.06**; −1.44	incomplete sepn. from Hg wave; 63		+0.11** in 0.1 *M* KHF_2 (Ref. 169)
Fe(III)	−0.52 (III → II)	140	−0.77 (III → II)	160		−0.74 (III → II)
			−1.47 (II → 0)	100		−1.44 (II → 0) in 1 *M* KF pH 7 (Ref. 170)
Ga(III)	N.R.		−1.50	about 120		
Mn(II)	N.R.		−1.55	about 40	−1.55 (pH 2.4 to 6.8)	
Mo(VI)	−0.53 (VI → V) I.S.H.W. (V → III)	130	N.R.			
Ni(II)	−1.00	61	−1.05	71	−1.12 (pH 4.3 to 6.4)	
Pb(II)	−0.40	28	−0.45	30	−0.41 (pH 1.1 to 2.8)	
Re(VII)	I.S.H.W.		about −1.44[m]			
Sb(III)	−0.62	100	−0.74	95	small prewave −0.68 (pH 3.0 to 4.4)	

TABLE 10 (continued)

Sb(V)	Reduced chemically by Hg to Sb(III); −0.65	90	I.S.A.W.§			
Se(IV)			−1.28	100		
Sn(II)	−0.23**; −0.60	−33; 27	−0.41**; −0.70	−34; 29	−0.20**; −0.73 (pH 4.0 to 6.3)	
Te(IV)			−0.52	140	−0.48 (pH 4.4)	
Ti(IV)	I.S.H.W.		−1.37	95		
Tl(I)	−0.46	54	−0.46	54	−0.50 (pH 3.7 to 6.7)	
U(VI)	−0.51	270	−0.80; −1.11	v. irr. waves		−0.94 (VI → V) in 1M NaF (Ref. 171)
V(IV)	I.S.H.W.		−1.45; about −1.68	irr. waves		
V(V)			about −0.12[m]; −0.79; −1.40 First 2 waves small	v. irr.; 140; 100		
Zn(II)	−1.11	35	−1.15	54	−1.14 (pH 4.2 to 6.4)	

m means a maximum
[a]N.R. means no reduction
* I.S.H.W. means incomplete separation from H^+ wave
** oxidation wave
§ I.S.A.W. means incomplete separation from NH_4^+ wave

In 0.1 *M* HF - 0.1 *M* NH_4F, in addition to the information given above, waves incompletely separated from the H^+ wave were found for chromium(III), indium, and tungsten(VI). No reduction before the hydrogen ion wave occurred with tin(IV) and niobium(V). In 1 *M* NH_4F (pH 7), waves incompletely separated from the NH_4^+ wave were found for chromium(III), niobium(V), tin(IV), and tungsten(VI). No reduction before the NH_4F wave occurred with indium, selenium(VI), tantalum, and zirconium.
The polarographic ranges in 0.1 *M* hydrofluoric acid – 0.1 *M* ammonium fluoride and in 1 *M* ammonium fluoride (pH 7) were +0.1 to −1.2 V vs. S.C.E. and +0.1 to −1.8 V vs. S.C.E., respectively.

TABLE 11

Voltammetric Data for Inorganic Species in 1 M Ammonium Fluoride

Species	$E_{1/2}$, V vs. S.C.E.	$E_{3/4} - E_{1/4}$ mV
Ferrocyanide	+0.18	56
Silver(I)	+0.21	−32*
Antimony(V)	+0.34	−122*
Iron(II)	+0.46	185
Iodide	+0.47[m]	
Manganese(II)	+0.52	28
Vanadium(IV)	+0.56	158
Thallium(I)	+0.87	95

*Reduction wave
[m]Maximum present

The oxidation wave for cobalt(II) started at +0.85 V and was not completed before the final rise in current.

There were no oxidation or reduction waves for antimony(III), arsenic(III) or (V), bromide, chromium(III) or (VI), copper(II), iron(III), nickel(II), and vanadium(V) at potentials more positive than 0 V vs. S.C.E.

With the rotating platinum electrode in 1 M ammonium fluoride the final rise in current occurred at +1.1 V vs. S.C.E.

(From Hamza, A. G. and Headridge, J. B., *Talanta*, 13, 1397 (1966). With permission.)

In the complexometric titration of zinc with EDTA, aluminum, calcium, and magnesium are masked by the addition of ammonium fluoride.[176] Aluminum forms a stable fluoro complex, while calcium and magnesium are precipitated as insoluble fluorides.

In the spectrophotometric determination of cobalt as tetraphenylarsonium thiocyanatocobaltate after extraction from aqueous solution into chloroform, interference from iron(III) resulting from formation of the red ferric thiocyanate complex is prevented by adding ammonium fluoride to the aqueous phase.[177]

B. Atomic Absorption Spectroscopy

Hydrofluoric acid is widely used to hold elements such as niobium, tantalum, and tungsten in solution prior to determination by atomic absorption spectroscopy. This use has been mentioned in Section III A1. However, the presence in solution of fluoride ion, and particularly ammonium fluoride, also increases the sensitivities of the atomic absorption method for zirconium, hafnium, titanium, tantalum, and uranium using the nitrous oxide-acetylene flame.[178] These are the elements that form stable oxide molecules in flames, but that exist in aqueous fluoride solution as stable fluoro complexes and that form volatile fluorides. In the determination of zirconium the presence of 0.1 M ammonium fluoride leads to an eightfold improvement in the sensitivity and causes interference effects to be either eliminated or appreciably suppressed.

C. The Separation of Silicon by Volatilization as Tetrafluoride

Silicon can be separated from most other elements by microdiffusion as silicon tetrafluoride from a mixture of hydrofluoric and sulfuric acids. The diffusion is allowed to proceed for 6 hr at room temperature. The silicon tetrafluoride is absorbed in ethylene glycol and the silicon is determined spectrophotometrically by the molybdenum-blue method.[179,180] The speed of this method can be increased by transferring the volatile silicon tetrafluoride from the sample solution at 70° C to an absorbing solution of ammonium molybdate by a current of dry air.[181]

Stobart[182] has described a related method for the determination of traces of silicon in niobium, tantalum, molybdenum, and tungsten. The finely divided sample was dissolved in a mixture of hydrofluoric and nitric acids in a Teflon® distillation apparatus. Perchloric acid was then added and the silicon tetrafluoride was distilled into a boric acid solution, in which the silicon was subsequently determined spectrophotometrically by the molybdenum-blue method. The method can also be applied to the determination of silicon in steels and copper-base samples.[183]

X. CONCLUSIONS

It is noted from the previous pages that hydrofluoric acid and fluorides have been employed in analytical chemistry for well over a century. The chief use of the fluoride ion is as a complexing agent; when the time was ripe for the development of analytical techniques such as ion-exchange and solvent-extraction separations and inorganic polarography, it was only natural that investigators should try to use the unique complexing properties of that ion to develop new analytical methods involving these techniques. Of course,

such work was inhibited to an appreciable extent until about 1955, when suitable plastic materials, unattacked by hydrofluoric acid, became readily available. By the use of fluoride, many satisfactory separation schemes involving ion-exchange resins have now been developed for the most complex materials containing elements such as zirconium, niobium, tantalum, molybdenum, and tungsten. By solvent extraction followed by a spectrophotometric finish, very selective methods have been developed for the determination of boron and tantalum.

The high stabilities of fluoro complexes provide the basis of many analytical methods and a reasonable amount of data on the stability constants of fluoro complexes is available. However, further research in this field would still be worthwhile to obtain a more comprehensive list of stability constants.

Work on the development of new redox titrations in fluoride media and on polarography and voltammetry in fluoride solutions is of interest to the analytical chemist as illustrating how theoretical predictions can be put to use in developing new methods of analysis. Undoubtedly, however, the most useful contributions in recent years have been in the dissolution of materials in fluoride media followed by atomic absorption spectroscopic analyses of the resulting solutions. The analytical chemist should be a realist and welcome anything that simplifies and speeds up an analysis. Dissolution procedures involving hydrofluoric acid and Teflon®-lined bombs followed by atomic absorption spectroscopy have greatly simplified silicate rock analysis and much activity in this field is to be expected in the future.

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Section 2. Electrochemical investigations with emphasis on non-aqueous solvents

14

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THE POLAROGRAPHY OF MOLYBDENUM, TITANIUM AND NIOBIUM IN SOLUTIONS OF ORGANIC ACIDS

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Polarography is an attractive analytical technique if it can be applied without any preliminary separations. With this in mind, it was decided to investigate further the polarographic reduction of molybdenum(VI), titanium(IV) and niobium(V) in order to develop rapid polarographic methods for the determination of these elements in niobium, tantalum and tungsten base alloys.

Recently HEADRIDGE AND HUBBARD[1] reported that molybdenum can be determined in certain niobium base alloys by a simple polarographic method using 0.5 *M* hydrofluoric acid–0.5 *M* sulphuric acid as base electrolyte. That method does, however, require a Teflon dropping mercury electrode and these are not commercially available. In addition it would be advantageous to determine not only molybdenum but also titanium and niobium in such high-temperature alloys, and this is not possible with the fluoride base electrolyte. It was proposed to dissolve the alloys in a mixture of hydrofluoric and nitric acids, add sulphuric acid, heat to fumes of sulphur trioxide, and then dilute with a solution of an organic acid to give the base electrolyte for polarography, since the organic acids form soluble complexes with niobium, tungsten, etc.

Previous polarographic investigations on niobium(V) in solutions of citric acid[2,3], EDTA[2,3], and tartaric, oxalic, lactic, malic and gluconic acids[2] have been reported, and the polarography of titanium(IV) in EDTA solution has been studied[4]. However, in these papers, little information is given on interfering elements and further investigations on these organic acid supporting electrolytes are reported in this paper.

EXPERIMENTAL

Apparatus

A Sargent model XV polarograph was used. A Meites-type H-cell was employed with a solution compartment for *ca.* 40 ml of solution. This compartment was connected to a saturated calomel electrode by means of an agar-saturated potassium chloride bridge.

Reagents

Citric, lactic, hydrofluoric, nitric and sulphuric acids, sodium hydroxide, thorium nitrate and the disodium salt of EDTA were all of analytical reagent grade. Other organic acids were of the purest grade available.

Standard molybdenum(VI) solution. A suitable weight of Specpure molybdenum trioxide (Johnson, Matthey and Co. Ltd.) was dissolved in boiling ammonia solution, s.g. 0.88, the solution was evaporated to dryness, and the residue dissolved in a citric–sulphuric acid mixture such that, on dilution, the final concentrations were 1 *M* citric acid and 0.1 *M* sulphuric acid. Less concentrated solutions of molybdenum were prepared from this solution.

Standard niobium(V) solution. A suitable weight of Specpure niobium pentoxide was dissolved in hot concentrated hydrofluoric acid. A calculated volume of concentrated sulphuric acid was added and the solution heated to fumes of sulphur trioxide. The cooled solution was added to an aqueous solution of citric acid, such that, on dilution, the final concentrations were 1 *M* citric acid and 0.5 *M* sulphuric acid.

Standard titanium(IV) solution. This was prepared from Specpure titanium metal in a similar manner to that used for the niobium(V) solution, except that a hot mixture of concentrated hydrofluoric and nitric acids was used to dissolve the metal.

Standard tungsten(VI) solution. This was prepared from Specpure tungsten trioxide in a similar manner to that used for niobium(V) solution, except that the tungsten trioxide was first dissolved in boiling ammonia solution, the solution evaporated to dryness and the residue dissolved in hot concentrated hydrofluoric acid before the addition of concentrated sulphuric acid.

Solutions of molybdenum, niobium and titanium in other organic acids were prepared in a similar manner.

RESULTS AND DISCUSSION

EDTA

A base electrolyte containing 0.05 *M* EDTA and 0.25–0.5 *M* sulphuric acid adjusted to pH 3.6 was found to be satisfactory for the determination of both titanium(IV) and niobium(V). At this pH the half-wave potentials are respectively −0.32 V and −0.65 V *vs.* S.C.E., which is in good agreement with previous studies[2,4]. Unfortunately, at this pH, molybdenum(VI) interferes by producing 2 waves covering the range of −0.34 V to −0.85 V *vs.* S.C.E. This is in accord with the findings of PECSOK AND SAWYER[5]. No EDTA base electrolyte could be found for the analysis of a mixture of molybdenum, titanium and niobium.

Citric acid

Investigations made for molybdenum(VI) and niobium(V) in various base electrolytes containing citric and sulphuric acids and their salts, in conjunction with the information given by KENNEDY[3], indicate that a mixture of molybdenum(VI) and niobium(V) is best determined in a citric acid base electrolyte of pH 2.4–3.6. The polarography of titanium(IV) in citric acid base electrolytes has been studied by PECSOK[6] and VANDERBOSCH[7] and their results combined with those above, would suggest that a mixture of molybdenum(VI), titanium(IV) and niobium(V) could be determined polarographically with 0.5 *M* citric acid in the pH range 2.4–3.6, the first wave being due to the reduction of molybdenum(VI) to molybdenum(V), the second to molybdenum(V) to molybdenum(III) plus titanium(IV) to titanium(III), and the third to niobium(V) to niobium(IV). The titanium would be determined by subtracting $2 \times \mathrm{Mo}(6\rightarrow5)$ from $\mathrm{Mo}(5\rightarrow3) + \mathrm{Ti}(4\rightarrow3)$.

In practice, however, no satisfactory wave could be obtained for titanium(IV) at pH 2.4–3.6 in the presence of citric and sulphuric acids. The sulphate ion was obviously interfering. For example, at pH 2.45 (1 *M* citric acid–0.5 *M* sulphuric acid) the titanium wave started at −0.60 V *vs.* S.C.E. with the diffusion current increasing rapidly as for a reversible reduction wave. But, then, the slope decreased and the plateau was not reached until the potential was −1.15 V *vs.* S.C.E. The wave probably consisted of 2 waves, a reversible reduction wave for a titanium–citrate complex surmounted by an irreversible wave for a titanium–sulphate complex.

It was, therefore, decided to try to suppress the interfering effect of sulphate ions by adding an excess of thorium nitrate to the solution. Thorium nitrate is a suitable complexing agent for sulphate[8] and good titanium reduction waves were found in base electrolytes consisting of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate in the pH range 2.0–3.5. The effect of thorium nitrate on the titanium wave is illustrated in Fig. 1 where 2 polarograms are recorded for solutions of pH 2.0. Polarographic data for molybdenum(VI), titanium(IV) and niobium(V) in the above base electrolyte adjusted to pH 3.5 are given in Table I.

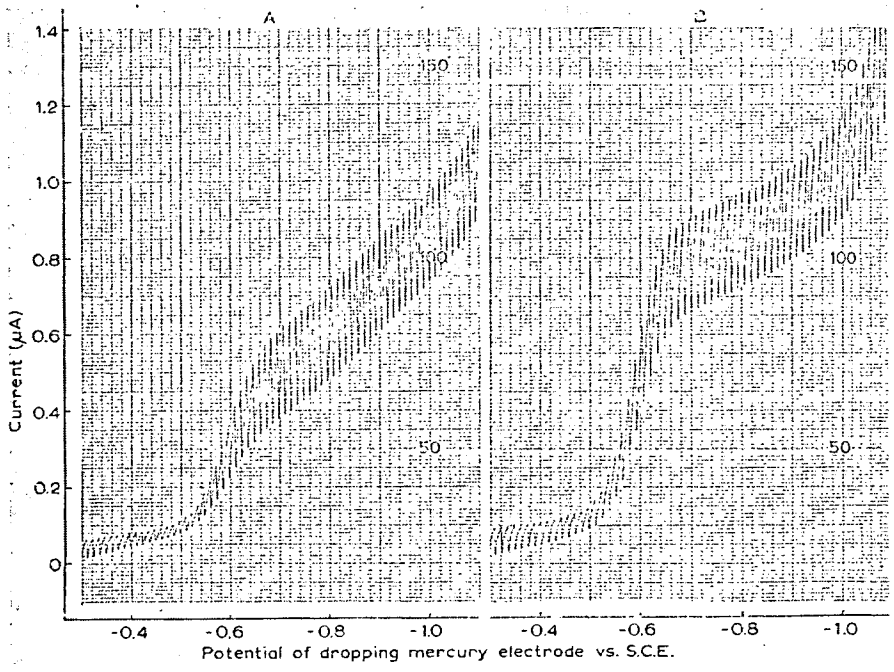

Fig. 1. Polarograms for $2.5 \cdot 10^{-4}$ *M* solutions of titanium(IV) in base electrolytes of (A) 0.5 *M* citric acid—0.025 *M* sulphuric acid adjusted to pH 2.0, and (B) 0.5 *M* citric acid—0.025 *M* sulphuric acid—0.05 *M* thorium nitrate adjusted to pH 2.0.

Unfortunately, the addition of thorium nitrate to the base electrolyte caused the hydrogen ion wave to occur earlier to the extent of about 0.1 V and the niobium(V) wave was no longer separated sufficiently from the hydrogen ion wave to allow a precise determination of niobium by d.c. polarography. The thorium nitrate had no effect on the molybdenum waves.

A method is, however, available for the determination of molybdenum and titanium in the presence of niobium.

In 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5, the diffusion current was directly proportional to the molybdenum(VI) concentration in the range $1.5 \cdot 10^{-5}$–$1.5 \cdot 10^{-4}$ *M*. In this range the standard deviation of the error in the diffusion current was 0.0025 μA, which corresponds to a relative standard deviation of 0.6% at a molybdenum concentration of $1.5 \cdot 10^{-4}$ *M*.

TABLE I

POLAROGRAPHIC DATA FOR MOLYBDENUM(VI), TITANIUM(IV) AND NIOBIUM(V) IN 0.5 *M* CITRIC ACID –0.025 *M* SULPHURIC ACID–0.05 *M* THORIUM NITRATE ADJUSTED TO PH 3.5

Species	$E_{\frac{1}{4}}$ *vs. S.C.E.* *(V)*	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ *(mV)*
Molybdenum(VI)	−0.273	96
	−0.635	72
Titanium(IV)	−0.698	69
Niobium(V)	Approx. −1.00	Approx. 80

Diffusion currents were measured on the plateau of the first molybdenum wave at a potential of −0.48 V *vs.* S.C.E. The error in diffusion current is expressed by i_d (measured) $- i_d$ (calculated) where the values of i_d (calculated) are points exactly on the straight line calibration graph of diffusion current *vs.* concentration.

With regard to titanium(IV) in the same base electrolyte, the diffusion current was again directly proportional to titanium concentration in the range $5 \cdot 10^{-5}$–$5 \cdot 10^{-4}$ *M*. In this range the standard deviation of the error in the diffusion current was 0.0095 μA, which corresponds to a relative standard deviation of 0.9% at a titanium concentration of $5 \cdot 10^{-4}$ *M*. Diffusion currents were measured on the plateau of the titanium wave at a potential of −0.85 V *vs.* S.C.E.

The diffusion current constant for molybdenum(VI) in the above base electrolyte was 1.21, the rate of flow of mercury (m) being 2.309 mg/sec and the drop time (t) being 3.871 sec. The diffusion constant for titanium(IV) was 0.97 with m at 2.310 mg/sec and t at 3.798 sec. Maximum currents were used in these calculations.

A method involving the base electrolyte 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5 was then developed and applied to the determination of molybdenum in a niobium base alloy, which contained no titanium. The method is outlined below. The molybdenum content of the alloy (nominal composition 15% tungsten, 5% molybdenum and 1% zirconium) was found by the polarographic method to be 4.63% with a standard deviation of 0.09%. The molybdenum content of the alloy determined spectrophotometrically using thiocyanate[9] was 4.65%.

The precision of this determination is satisfactory but would have been even better with a more sensitive polarograph. It was not possible to acquire suitable alloys for evaluating the method for the determination of titanium, and molybdenum plus titanium in niobium base alloys, but there seems no reason why titanium could not be determined. With molybdenum present, titanium could not, of course, be determined as precisely as in its absence, since for solutions containing both molybdenum and titanium, the diffusion current for titanium is obtained by subtraction.

Tungsten(VI), tantalum and zirconium are reduced well after the titanium

wave and do not interfere with the determination of molybdenum and titanium. More than trace amounts of iron(III) interfere with the determination of molybdenum(VI) using the first wave. The reduction wave for chromium(III) occurs well after the first molybdenum wave but interferes with the determination of titanium(IV). There is no interference from nickel.

Method for the determination of molybdenum in niobium base alloys

Dissolve about 200 mg of alloy, accurately weighed, in 5 ml of concentrated nitric acid plus 10 ml of concentrated hydrofluoric acid in a platinum crucible. Add 2.77 ml of concentrated sulphuric acid from a burette and heat the solution to fumes of sulphur trioxide. Add the contents of the crucible to *ca.* 50 ml of water containing 21.02 g of citric acid monohydrate crystals in a beaker and dilute the solution to 100 ml in a graduated flask.

Pipette 5 ml of the solution into a beaker and add 45 ml of 1 *M* citric acid solution and 30 ml of water. Adjust the pH to within the range 2.0–3.0 with 10 *M* sodium hydroxide solution and add 2.94 g of thorium nitrate hexahydrate crystals. Stir to dissolve the crystals, add sodium hydroxide solution until the pH is exactly 3.5 and dilute the solution to 100 ml in a graduated flask.

Place approximately 40 ml of this solution in the polarographic cell and deoxygenate by bubbling oxygen-free nitrogen through it for 10 min. Record a polarogram from 0 to −1.0 V *vs.* S.C.E. Measure the diffusion current for the first molybdenum wave at an applied potential of −0.48 V *vs.* S.C.E. and read the concentration of molybdenum in the solution from a calibration graph prepared with standard solutions of molybdenum examined polarographically under the same conditions as for the alloy.

(For the alloy, the calibration graph mentioned above, for verification that the diffusion current was directly proportional to concentration, was used.)

Other organic acids

Polarograms for base electrolytes containing lactic or glycollic acid were unsatisfactory since both acids obviously contained reducible impurities. No further work was done with these.

With gluconic acid, a good reduction wave for niobium(V), $E_{\frac{1}{4}} = -1.04$ V *vs.* S.C.E., was obtained in the base electrolyte, 0.3 *M* gluconic acid–0.5 *M* sulphuric acid adjusted to pH 4.3. In this base electrolyte, titanium(IV) produced a wave, $E_{\frac{1}{4}} = -0.99$ V *vs.* S.C.E., but the upper part of the wave was drawn out, indicating that sulphate was again having an undesirable effect. Under the same conditions, molybdenum(VI) produced 3 overlapping reduction waves with half-wave potentials of approximately −0.47, −0.60 and −0.80 V *vs.* S.C.E.

It was therefore concluded that none of the other organic acids which were examined, was likely to be as satisfactory as citric acid as base electrolyte for the polarographic determination of molybdenum and titanium in the presence of niobium.

CONCLUSIONS

Although the object of this study, namely the development of a polarographic method for the simultaneous determination of molybdenum, titanium and niobium in alloys containing these elements and zirconium, tantalum and tungsten was not

achieved, it was shown that a base electrolyte of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5 should be suitable for the determination of molybdenum and titanium in niobium base alloys. This base electrolyte should also be satisfactory for the determination of molybdenum and titanium in tungsten base and tantalum base alloys. In the absence of titanium, the thorium nitrate can be omitted and a base electrolyte of 1 *M* citric acid–0.5 *M* sulphuric acid adjusted to pH 2.4–3.6 is suitable for the determination of both molybdenum and niobium.

We are indebted to the British Iron and Steel Research Association for providing one of us (D.P.H.) with a maintenance grant.

SUMMARY

Further work on the polarographic reduction of molybdenum(VI), niobium(V) and titanium(IV) in base electrolytes containing organic acids is reported. A base electrolyte of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate proved suitable for the determination of molybdenum and titanium in the presence of niobium, tantalum, tungsten and zirconium. A direct polarographic method using this base electrolyte is described for the determination of molybdenum in a niobium base alloy.

RÉSUMÉ

Les auteurs ont examiné la réduction polarographique du molybdène(VI), du niobium(V) et du titane(IV) dans des électrolytes de base renfermant des acides organiques. Le mélange acide citrique 0.5 *M*, acide sulfurique 0.025 *M* et nitrate de thorium 0.05 *M* convient au dosage du molybdène et du titane, en présence de niobium, tantale, tungstène et zirconium. Une méthode est proposée pour le dosage du molybdène dans un alliage à base de niobium.

ZUSAMMENFASSUNG

Über die polarographische Reduktion von Molybdän(VI), Niob(V) und Titan(IV) in Grundelektrolyten, die organische Säuren enthalten, wird berichtet. Ein Grundelektrolyt mit 0.5 *M* Citronensäure, 0.025 *M* Schwefelsäure und 0.05 *M* Thoriumnitrat ist für die Bestimmung von Molybdän und Titan in Gegenwart von Niob, Tantal, Wolfram und Zirkonium geeignet. Es wird eine direkte polarographische Methode, die diesen Grundelektrolyten verwendet, für die Bestimmung von Molybdän in einer Niobiegierung beschrieben.

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Polarography of Inorganic Compounds in Acetic Acid–Acetic Anhydride Solution

By J. B. Headridge and D. Pletcher

Polarographic data for 23 inorganic species in acetic acid–acetic anhydride (20:1, v/v) are reported, the base electrolytes being 0·25M-sodium perchlorate, 0·25M-sodium acetate, and 0·25M-lithium chloride. Evidence is presented to show that inorganic ions are solvated less readily in the organic solvent than in aqueous solution, but the order of reduction of ions is similar to that for aqueous solutions, with the exception of nickel, which is reduced much more readily in the non-aqueous solvent. Both acetate and chloride ions are moderately good complexing agents for inorganic ions in the organic solvent.

POLAROGRAPHIC investigations on the reduction of inorganic ions in many aqueous base electrolytes have been extensive,[1] but much less information of analytical interest is available for non-aqueous solutions. The polarography of inorganic compounds in non-aqueous solvents such as acetonitrile,[2] dimethylformamide,[3] and ethylenediamine[4] has been studied, but from the analytical standpoint these solvents are usually unsuitable because the materials to be analysed are seldom soluble in them, and too much preliminary work would be necessary to get the materials into a soluble form. However, materials for analysis can easily be obtained as aqueous solutions and a solution of the inorganic ions in acetic acid–acetic anhydride is readily obtained by adding an excess of acetic anhydride to the aqueous solution and refluxing until reaction between water and acetic anhydride is complete.

Because the free energy of solvation of inorganic ions is, naturally, dependent in the solvent, the half-wave potentials of reversible waves for a particular ion in various solvents are different, and such shifts in half-wave potential can be of analytical significance. Also, the degree of irreversibility of waves frequently changes with the solvent, and troublesome hydrolytic reactions do not occur in non-aqueous solvents. For these reasons, a polarographic investigation of inorganic compounds in acetic acid–acetic anhydride (20 : 1, v/v) was undertaken.

Previous polarographic studies in glacial acetic acid have been made for a limited number of ions,[5-7] but a much more detailed investigation is reported here.

EXPERIMENTAL

Sodium perchlorate was prepared from microanalytical reagent grade sodium carbonate and analytical reagent grade perchloric acid, and was dried at 200°. Sodium acetate was analytical reagent grade dried at 120°. Lithium chloride was 99% pure lithium chloride dried at 200°.

Acetic acid–acetic anhydride solution was prepared from analytical reagent grade acetic acid which had been refluxed for 10 hr. over 5% (w/v) chromium trioxide and distilled three times, and analytical reagent grade acetic anhydride, twice distilled. Purified acetic anhydride (40 ml.) was added to purified acetic acid (1 l.) and the mixture refluxed for 2 hr. The ratio of acetic acid to acetic anhydride in the refluxed mixture was about 25 : 1 (v/v). The acetic anhydride content of the mixture was determined by measuring its optical density in a 1-cm. cell against glacial acetic acid in a reference cell at 275 mμ, and referring to a suitable calibration graph. The ratio of acetic acid to acetic anhydride was then adjusted to exactly 20 : 1 (v/v) by the addition of the calculated volume of acetic anhydride. The wavelength scale of the spectrophotometer was set to exactly the same position each time (275 mμ) by rotating the wavelength control knob until the optical density of a 0·2774M-solution of sodium nitrate in a 1-cm. cell was exactly 0·760.

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Base Electrolytes.—0·25M-Sodium perchlorate and 0·25M-lithium chloride were prepared by dissolving the salts in the organic mixture. In order to obtain a purified 0·25M-solution of sodium acetate in the organic mixture, a column (30 cm. × 7 cm.²) of De-Acidite FF resin (Grade SRA 70) in the acetate form was prepared in acetic acid–acetic anhydride (20 : 1, v/v), and 0·25M-sodium acetate (1 l.) in the organic mixture was passed through the column. The effluent was employed as base electrolyte. By this procedure most of the trace impurity of sulphate in the solution was removed.

Apparatus.—A Sargent model XV d.c. recording polarograph was used.

The following Meites (type H) cells were employed, the organic solvent being used throughout.

Cell A, for use with sodium perchlorate base electrolyte. The reference electrode was mercury–mercurous chloride–1M-lithium chloride saturated with methyl-cellulose, hereafter called reference electrode A. The salt bridge consisted of a gel of 0·25M-sodium perchlorate containing 7·5% (w/v) of methyl-cellulose. The cell resistance was 7200 ohms.

Cell B, for use with sodium acetate base electrolyte. The reference electrode was mercury–mercurous acetate–saturated lithium acetate saturated with methyl-cellulose. The salt bridge consisted of a gel of saturated lithium acetate containing 3·5% (w/v) of methyl-cellulose. The cell resistance was 10,000 ohms.

Cell C, for use with lithium chloride base electrolyte. The reference electrode was the same as that employed in cell A. The salt bridge consisted of a gel of 1M-tetraethylammonium chloride containing 5% (w/v) of methylcellulose. The cell resistance was 5400 ohms.

Solutions in the polarographic cell were deoxygenated with a stream of dry oxygen-free nitrogen. The cells were immersed in a water-bath thermostated at 25·0°.

TABLE 1

		Base electrolyte					
		0·25M-$NaClO_4$		0·25M-NaOAc		0·25M-LiCl	
Species	Compound used	$E_{\frac{1}{4}}$ (v)	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ (mv)	$E_{\frac{1}{4}}$ (v)	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ (mv)	$E_{\frac{1}{4}}$ (v)	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ (mv)
Silver(I)	AgOAc	>+0·6	—	>+0·4*	—	>0	—
Vanadium(V)	$NaVO_3,4H_2O$	—	—	(1) >+0·4*	—	(1) >0	—
				(2) Wave from −0·6 onwards	—	(2) −0·307	52
						(3) Wave from −0·4 onwards	
Antimony(V)	$SbCl_5$	—	—	(1) >+0·2*	—	(1) >0	
				(2) −0·14	30	(2) −0·122*	19(R)
				(3) −0·28	59		
Iron(III)	†	>+0·6*	—	(1) +0·17	73	>0	—
				(2) −0·08	77		
Copper(II)	$Cu(OAc)_2,H_2O$	+0·43*	65	+0·172*	36	(1) >0	—
						(2) −0·193*	57(R)
Molybdenum(VI)	$Na_2MoO_4,2H_2O$	—	—	(1) +0·16*	145	(1) >0	—
				(2) −0·40	185	(2) −0·179	65
Bismuth(III)	$(BiO)_2CO_3,\frac{1}{2}H_2O$	—	—	−0·040*	87	−0·060	24
Tin(II)	$SnCl_2,2H_2O$	(1) +0·11	−34	(1) +0·061	−35	(1) −0·03	—
		(2) −0·20	38	(2) −0·386	36(R)	(2) −0·451	28(R)
Tin(IV)	$SnCl_4$	—	—	Wave from −0·4 onwards	—	(1) −0·05	—
						(2) −0·445	28(R)
Uranium(VI)	$UO_2(OAc)_2,2H_2O$	−0·04*	83	−0·280	44	>−0·1*	—
Antimony(III)	$SbCl_3$	—	—	(1) −0·14*	38	−0·124*	20(R)
				(2) −0·29	53		
Lead(II)	$Pb(OAc)_2,3H_2O$	−0·14*	34	−0·288	28(R)	−0·375	27(R)
Thallium(I)	TlOAc(aq.)	−0·29	60(R)	−0·320	79	−0·393	54(R)
Cadmium	$Cd(OAc)_2,2H_2O$	−0·25	42	−0·417	31(R)	−0·587	30(R)
Europium(III)	Eu_2O_3	—	—	−0·68	145	−0·330	59(R)
Nickel(II)	$Ni(OAc)_2$	−0·65	110	−0·692	94	−0·336	47
Indium(III)	In_2O_3	N.R.	—	−0·814	37	−0·524	22(R)
Zinc(II)	$Zn(OAc)_2,2H_2O$	−0·60	74	−0·844	50	N.R.	—
Chromium(III)	$CrCl_3,6H_2O$	(1) −0·63	120	N.R.	—	N.R.	—
		(2) Wave from −0·8 onwards	—				
Cobalt(II)	$Co(OAc)_2$	−0·84	—	−0·94	100	−0·9	—
Niobium(V)	$NbCl_5$	—	—	Wave from −0·8 onwards	—	Wave from −0·4 onwards	—
Tungsten(VI)	WCl_6	—	—	Wave from −0·9 onwards	—	Wave from −0·4 onwards	—
Manganese(II)	$Mn(OAc)_2,4H_2O$	N.R.	—	N.R.	—	N.R.	—

* The maximum on this wave was suppressed by the addition of methyl-cellulose up to a maximum concentration of 0·002% (w/v) in the solution compartment of the cell. † Anhydrous ferric chloride in sodium perchlorate and lithium chloride solutions; ferric perchlorate decahydrate in sodium acetate solution. R = Reversible wave. N.R. = no reduction. "Wave from −*x* onwards" means that the reduction wave commenced at −*x* volts and was not completed before the final rise in current.

RESULTS

Polarographic data for 26 inorganic species in the three base electrolytes are given in Tables 1 and 2.

TABLE 2

Species	Diffusion-current constant 0·25M-$NaClO_4$	0·25M-NaOAc	0·25M-LiCl
Uranium(VI)	2·92	1·85	—
Antimony(III)	—	—	3·01
Lead(II)	3·27	2·80	—
Cadmium(II)	2·49	2·68	2·74
Nickel(II)	—	2·51	2·93
Zinc(II)	3·74	—	—

The concentrations of inorganic ions in the solutions were in the range (1—6) × 10^{-4}M except for solutions of europium(III), indium(III), silver(I), lead(II) (chloride medium), and thallium(I) (chloride medium), which were saturated ($< 2 \times 10^{-4}$M).

All $E_{\frac{1}{4}}$, $E_{\frac{1}{2}}$, and $E_{\frac{3}{4}}$ values were corrected for potential drop across the cell.

All $E_{\frac{1}{2}}$ values are given with respect to reference electrode A (see Experimental section). The potential of the mercury–mercurous acetate–saturated lithium acetate electrode was +0·430 v *versus* reference electrode A.

The half-wave potentials in perchlorate base electrolyte are quoted only to the nearest 10 mv because they became slightly more negative with time. Methyl-cellulose, diffusing into the solution from the salt bridge, is probably the cause of this effect, if it is assumed that it can form very weak complexes with metal ions in perchlorate solution. The drifts in half-wave potentials never exceeded 10 mv/hr. In contrast, $E_{\frac{1}{2}}$ values for ions in acetate and chloride solutions remained constant with time.

Maximum diffusion currents were used in calculating the diffusion-current constants in Table 2.

DISCUSSION

The usable polarographic ranges with the sodium perchlorate, sodium acetate, and lithium chloride base electrolytes were +0·6 to −1·0 v, +0·4 to −1·1 v, and 0 to −1·0 v, respectively, *versus* reference electrode A.

With the perchlorate and acetate base electrolytes, traces of sulphate ion produced a mercury oxidation wave, $E_{\frac{1}{2}} \sim +0{\cdot}2$ v *versus* reference electrode A. With the sodium perchlorate base electrolyte the sulphate wave did not interfere appreciably with any of the other inorganic ion waves, but in untreated sodium acetate base electrolyte it interfered seriously with the reduction waves of iron(III), copper(II), and molybdenum(VI). For this reason, a 0·25M-sodium acetate solution of much lower sulphate concentration was prepared by passing the untreated sodium acetate solution through a column of anion-exchange resin in the acetate form. However, even this purified acetate base electrolyte was not entirely free from sulphate ion and it was necessary to make allowance for the small sulphate wave, which remained, when obtaining polarographic data for ions that produced waves in the vicinity of the sulphate wave.

It can be seen from Table 1, by comparing half-wave potentials for reversible or nearly reversible waves, that both acetate and chloride are moderately good complexing agents for inorganic ions in acetic acid–acetic anhydride (20 : 1, v/v).

The fact that the half-wave potential of the nickel(II) wave in chloride solutions is more positive than in perchlorate solution is interesting and shows that, at a fixed potential, the rate of reduction is faster in chloride than in perchlorate solution. The rate of reduction of indium(III) in acetous perchlorate solution must be very slow since no wave is obtained before the final rise in current. In aqueous perchlorate solution the reduction wave for indium(III) is also very irreversible.

In order to obtain information about the relative solvating powers of acetic acid and water, it was necessary to convert the half-wave potentials for waves in the organic solvent *versus* reference electrode A into half-wave potentials *versus* the aqueous saturated calomel electrode (aq. S.C.E.), and compare these half-wave potentials with those for the same ions in the aqueous base electrolyte. Such a comparison is made in Table 3 for some reduction waves.

TABLE 3

Inorganic species	$E_{\frac{1}{2}}$ (v) for acetous 0·25M-$NaClO_4$ *vs.* the aq. S.C.E.	$E_{\frac{1}{2}}$ (v) for aqueous 0·25M-$NaClO_4$ *vs.* the aq. S.C.E.
Lead(II)	−0·16	−0·38 *
Tin(II)	−0·22	−0·39 *
Cadmium	−0·27	−0·58 *
Thallium(I)	−0·31 *	−0·45 *
Zinc	−0·62	−1·00 *

* Reversible reduction.

Unfortunately, only thallium(I) produced a reversible wave in acetous sodium perchlorate, the other ions being reduced irreversibly (see Table 1), but if these ions had been reduced reversibly, their half-wave potentials would have been even more positive than those listed. It is, therefore, obvious that the free energy of solvation of inorganic ions in the organic solvent is less than the free energy of solvation of these ions in water.

All half-wave potentials reported for ions in acetic acid–acetic anhydride solvent *versus* the aqueous S.C.E. are corrected for liquid-junction potential associated with the different solvents. This has been made possible by using Čihalík and Šimek's value [6] of −0·055 v for the potential of the mercury–mercurous chloride–saturated acetous lithium chloride reference electrode *versus* the aqueous S.C.E. where the liquid-junction potential between saturated aqueous potassium chloride and saturated acetous lithium chloride has been eliminated by Vlček's graphical method.[8] We have determined that our electrode of mercury–mercurous chloride–1M-lithium chloride in acetic acid–acetic anhydride, *i.e.*, reference electrode A, has a potential of +0·039 v *versus* the mercury–mercurous chloride–saturated acetous lithium chloride electrode, which means that the potential of reference electrode A is −0·016 v *versus* the aq. S.C.E. This value may be slightly in error, since our solvent is acetic acid–acetic anhydride (20 : 1, v/v) and not glacial acetic acid, and since Čihalík's measurements were made at 20° while ours were taken at 25°, but the error cannot be more than 20 mv.

[8] A. A. Vlček, *Coll. Czech. Chem. Comm.*, 1951, **16**, 230.

The order of reduction of inorganic ions in the organic solvent is similar to that in aqueous solution with a notable exception in nickel(II) in chloride base electrolyte, which reduces at a much more positive potential in the organic solvent than in water (−0·37 v *versus* the aq. S.C.E. in acetic acid–acetic anhydride, 0·25M in lithium chloride; −1·01 v *versus* the aq. S.C.E. in 0·25M-aqueous chloride). The polarographic reduction waves for cobalt and nickel in aqueous base electrolytes are seldom separated sufficiently to allow a satisfactory polarographic determination of these ions,[1] but we have found, as expected from the polarographic data reported in Table 1, that a nickel wave, well separated from the cobalt wave, is obtained by adding the appropriate amount of acetic anhydride to an aqueous lithium chloride solution, refluxing the mixture for 3 hours, and running a polarogram on the resulting non-aqueous solution.

It is interesting to note that tin(IV), niobium(V), and tungsten(VI), as chlorides, dissolve without precipitation in 0·25M-acetous lithium chloride, while in aqueous lithium chloride solution they are hydrolysed with the production of insoluble hydrated oxides. Well-defined polarographic waves were obtained for tin(IV) in 0·25M-acetous lithium chloride, and for niobium(V) in saturated acetous lithium chloride solution ($E_{\frac{1}{4}}$ is −0·52 v *versus* reference electrode A).

Diffusion current was directly proportional to lead concentration over the range of 5×10^{-5} to 5×10^{-4}M in 0·25M-acetous sodium acetate. The standard deviation of the error in diffusion current was 0·021 μA, which corresponds to a relative standard deviation of 0·8% at a lead concentration of 5×10^{-4}M. This relative standard deviation compares very favourably with similar statistical data obtained for aqueous base electrolytes. The error in diffusion current is expressed by i_d(obs.) − i_d(calc.), where the values of i_d(calc.) are points exactly on the straight-line calibration graph of diffusion current *versus* concentration. There is no reason to believe that diffusion current will not be directly proportional to concentration for other ions in the acetic acid–acetic anhydride base electrolytes.

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Polarography of Inorganic Substances in Anhydrous Sulpholan

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Polarographic and voltammetric results are reported for 22 inorganic substances in anhydrous sulpholan with 0·1M-perchlorates as base electrolytes and a reference electrode of silver–silver chloride–saturated tetraethylammonium chloride in sulpholan. The redox behaviour of these substances and their positions in the polarographic series are similar in sulpholan and aqueous solutions, with the interesting exceptions of bromide, oxygen, and certain of the rare-earth ions.

In the last decade, polarographic investigations of inorganic substances in several non-aqueous solvents have been undertaken,[1] but little information is available on polarography in sulpholan (tetrahydrothiophen 1,1-dioxide). Hills [2] stated that polarography in it is possible. Electrochemical studies have been made in solvents which solvate metallic ions through amine, cyanide, hydroxyl, ketonic, nitro, and sulphoxide groups, such as ethylenediamine, acetonitrile, ethanol, acetone, nitromethane, and dimethyl sulphoxide, respectively. We have now studied the polarography of 22 inorganic species in sulpholan, which solvates metallic ions through a sulphone group. Sulpholan, having a large liquid range (28—285°) and a high dielectric constant (44 at 30°), is a suitable solvent for polarography.

EXPERIMENTAL

Sulpholan (Shell Chemical Co.) was purified by an adaptation of Jones method [3] by distillation below 100° *in vacuo* (*a*) from solid sodium hydroxide, (*b*) from sulphuric acid plus hydrogen peroxide, (*c*) from solid sodium hydroxide, and (*d*) twice from calcium hydride.

Potassium, silver, magnesium, and barium perchlorates (B.D.H.) were dried in a vacuum oven at 100° (silver perchlorate at room temperature). Other perchlorates were prepared by well-established methods and dried *in vacuo* at room temperature.

Lithium salts were used to prepare solutions of chloride and bromide. The perchlorates of silver, thallium(I), cobalticinium, aluminium, barium, magnesium, sodium, rubidium, and potassium ions were anhydrous. The other perchlorates were hydrated.

The concentrations of all electroactive ions in the solutions being polarographed were within the range (0·5—3) $\times 10^{-3}$M.

All solutions were prepared and added to the polarographic cell in a glove-box.

All potentials are referred to the silver–silver chloride–saturated tetraethylammonium chloride reference electrode. $E_{\frac{1}{4}}$, $E_{\frac{1}{2}}$, and $E_{\frac{3}{4}}$ values are corrected for potential drop across the cell.

Base Electrolytes.—Solutions (0·1M) of lithium, sodium, and tetraethylammonium perchlorates were prepared by dissolution in sulpholan. Lithium perchlorate was prepared from lithium carbonate and AnalaR perchloric acid, recrystallised from water, and dried at 200°. Sodium perchlorate was prepared similarly except that microanalytical reagent grade sodium carbonate was used. Tetraethylammonium perchlorate (Eastman-Kodak) was dried in a vacuum oven at 60°.

Apparatus.—A Sargent model XV D.C. recording polarograph was used. A three-compartment H-cell was used throughout, the central horizontal cross-arm being separated from the vertical reference electrode compartment by a No. 3 sintered glass disc and from the vertical solution compartment by a No. 4 sintered glass disc. The reference electrode was a sheet of silver (5 × 2 cm.) coated with silver chloride and immersed in sulpholan saturated with silver chloride and tetraethylammonium chloride. The central compartment contained 0·1M-tetraethylammonium perchlorate in sulpholan. The solution compartment of 25 ml. capacity was fitted with a sintered glass dispersion tube for bubbling dry, oxygen-free nitrogen through the sulpholan solutions.

The cell was immersed in a bath of liquid paraffin, whose temperature was controlled at 40·0°. The resistance of the cell was 6300 ohms with 0·1M-sodium perchlorate in the solution compartment.

RESULTS

Polarographic and voltammetric results for 22 inorganic species in 0·1M-perchlorate solutions are in Table 1.

The polarographic ranges were +1·2 to −1·3 v and +1·2 to −2·3 v with 0·1M-sodium perchlorate and 0·1M-tetraethylammonium perchlorate base electrolytes, respectively. The voltammetric range was +3·3 to −1·3 v with 0·1M-sodium perchlorate base electrolyte.

Diffusion current was directly proportional to thallium concentration over the range of 5×10^{-4} to 5×10^{-3}M in 0·1M-sodium perchlorate. The standard deviation of the error in diffusion current was 0·048 μA, which corresponds to a relative standard deviation of 0·7% at a thallium concentration of 5×10^{-3}M. The error in diffusion current is expressed by i_d (obs.) $-i_d$ (calc.), where the values of i_d (calc.) are points exactly on the straight-line calibration graph of diffusion current against concentration.

The diffusion-current constant for thallium(I) was 0·86 with $m = 1·52$ mg./sec. and $t = 3·80$ sec., both measured at a potential of −0·1 v *versus* the reference electrode. Maximum diffusion currents were used in calculating the diffusion-current constant.

DISCUSSION

The relative standard deviation of 0·7% for the determination of thallium at a concentration of 5×10^{-3}M compares very favourably with similar statistical data obtained for aqueous base electrolytes. There is no

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TABLE 1

Species	Base electrolyte	$E_{\frac{1}{4}}$ (v)	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ (mv)
Chloride	$LiClO_4$	+2·53 *	−240
Bromide	,,	(1) +1·34 *	−260
		(2) +1·88 *	−150
Silver(I)	$NaClO_4$	+0·99 *	45
Ferrocene	,,	+0·83 *	−58 (R)
Copper(II)	,,	*ca.* +1·00 †	approx. 90
Europium(III)	,,	(1) +0·69	87
		(2) Wave not separated from final rise in current	—
Lead(II)	,,	*ca.* +0·38 †	—
Cadmium(II)	,,	+0·33	29 (R)
Nickel(II)	,,	+0·32	120
Thallium(I)	,,	+0·14	56 (R)
Zinc(II)	,,	+0·01	36
Oxygen	,,	(1) −0·04	63
		(2) −0·64	220
Cobalt(II)	,,	*ca.* −0·15 †	approx. 70
Cobalticinium ion	,,	−0·50	56 (R)
Samarium(III)	,,	(1) −0·51	70
		(2) −1·22	35
Manganese(II)	,,	−0·56	28 (R)
Aluminium(III)	,,	−0·64	140
Barium(II)	Et_4NClO_4	−1·33	41
Sodium(I)	,,	−1·44	64
Magnesium(II)	,,	−1·45	100
Rubidium(I)	,,	−1·53	66
Potassium(I)	,,	−1·55	67

* Determined voltammetrically with a rotating platinum electrode.

R, Reversible wave. † Wave showed a maximum.

reason to believe that diffusion current will not be proportional to concentration for other ions in sulpholan.

The diffusion-current constant of 0·86 for thallium is much smaller than that for thallium ion in aqueous 0·1M-sodium perchlorate solution (2·70 at 25° using the average diffusion current [4]). This results from the high viscosity of sulpholan (9·87 centipoise at 30°) compared with water (0·80 centipoise at 30°).

Bromide gave two very irreversible oxidation waves in the ratio of 2 : 1. These are probably due to the oxidation of bromine first to the tribromide ion and then to bromine. Kolthoff and Coetzee [5] found that bromide behaved similarly in acetonitrile. However, only one very irreversible wave was observed for the oxidation of chloride.

Two reduction waves of approximately equal height were obtained for oxygen. The first is most likely a result of the reduction of oxygen to the superoxide ion as occurs in many aprotic solvents.[6-8] The second may possibly be explained by the reaction $O_2^- + 2Na^+ + e \longrightarrow Na_2O_2$ as postulated by Johnson *et al.*[8] for the second reduction wave for oxygen in dimethyl sulphoxide.

With europium(III) and samarium(III), the first wave in Table 1 results from reduction to the 2+ state and the second from reduction to the amalgam. Of considerable interest are the differences between the half-wave potentials of the two samarium waves in sulpholan and in aqueous solution. These are 0·71 v for sulpholan solution (1·22—0·51) but only 0·16 v for aqueous solution (1·96—1·80).[9] Samarium(II) is certainly more readily produced from samarium(III) by reduction in sulpholan than in water. This is also true for acetonitrile.[10] It would be interesting to know if thulium(II) can be produced from thulium(III) by polarographic reduction in sulpholan (or acetonitrile); it cannot be produced by polarographic reduction of thulium(III) in aqueous solution.

Because in some cases the anhydrous metal perchlorates or anhydrous sulpholan adducts of these perchlorates could not be prepared, it is necessary to consider if the half-wave potential for the reversible reduction wave of an ion produced from the hydrated perchlorate is appreciably more negative than that of the solvated ion produced from the anhydrous salt. (Water is a complexing agent in many non-aqueous solvents.) For cadmium ion, which gives a reversible reduction wave in sulpholan, the effect of adding increasing amounts of water was investigated. The half-wave potentials of the reversible waves are shown in Table 2.

TABLE 2

Concn. of added water (M)	0·00	0·10	0·14	0·20	0·28	0·40
Half-wave potential (v)	0·333	0·298	0·286	0·275	0·259	0·246

The concentration of hydrated cadmium ion in solution was $1·3 \times 10^{-3}$M, *i.e.*, 8×10^{-3}M in water. We conclude that the effect on the half-wave potential of using hydrated perchlorates instead of anhydrous perchlorates is not appreciable. The difference in half-wave potentials between the reduction waves for anhydrous and hydrated cadmium perchlorates is not likely to exceed 0·01 v.

Although anhydrous perchlorates of some ions could not be made, anhydrous cadmium and zinc nitrates were readily prepared.[11] Polarograms were obtained for approximately 10^{-3}M solutions of these nitrates in 0·1M-sodium perchlorate in sulpholan. These show, however, that the nitrate ion forms complexes with these ions, which are reduced at more negative potentials and less reversibly than hydrated cadmium and zinc perchlorates.

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The polarographic behaviour of rare-earth ions in benzonitrile

The polarographic behaviour of rare-earth ions has been investigated in several non-aqueous solvents, *e.g.*, acetone[1], acetonitrile[2], dimethylformamide[3], dimethylsulphoxide[3], and ethylenediamine[4]. It is clear from these papers that in acetone and acetonitrile (solvents with lower solvating powers than water) the divalent ions, europium(II), samarium(II), and ytterbium(II), are more stable than in aqueous solution. Since neodymium(II) and thulium(II) have been reported to exist in the solid state[5], it seems possible that these divalent states could be stable in a solvent of very low solvating power. Benzonitrile is such a solvent[6], and in this communication polarographic data for some rare earth-ions in benzonitrile are reported.

Experimental

Acetonitrile was purified by the method of FORCIER AND OLVER[7], and the benzonitrile by distillation from calcium hydride. The water content of both solvents was determined by a modified Karl Fischer titration[8] and in both cases it was below the minimum determinable [$2 \cdot 10^{-3}$ M].

Tetraethylammonium perchlorate was obtained from Eastman Kodak and dried at 60° under high vacuum. The rare-earth perchlorates were prepared from 99.9% pure oxides obtained from Johnson Matthey & Co. Ltd., and A.R. perchloric acid. The oxide was dissolved in an equivalent quantity of perchloric acid and the solution heated to dryness on a hot plate. The perchlorate was then taken up in approximately 5 ml of water, the solution adjusted to pH 3, and the water removed under high vacuum at room temperature.

Apparatus and procedure

A Sargent Model XV d.c. recording polarograph was used.

The cell used is shown in Fig. 1. When filled throughout with 0.1 M tetra-

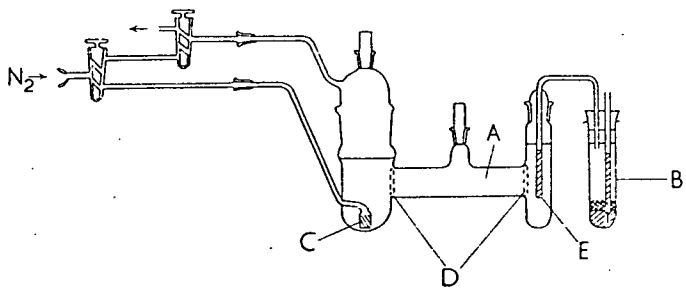

Fig. 1. (A), 0.1 M Et_4NClO_4 in the organic solvent; (B), aq. S.C.E.; (C), degassing sinter; (D), sinters, porosity No. 4; (E), aqueous gel of 3.5% (w/v) agar in 0.1 M $NaClO_4$.

ethylammonium perchlorate in acetonitrile, the cell had a resistance of 1,200 Ω, and when filled with 0.1 M tetraethylammonium perchlorate in benzonitrile, its resistance was 4,100 Ω. All solutions were prepared in a glove box. The polarograms were run with the cell immersed in a bath thermostatically controlled at 25°. The solutions were deoxygenated with a fast stream of oxygen-free, dry nitrogen which had been pre-saturated with the solvent being used.

Results

Polarographic data for the rare-earth ions in water, acetonitrile, and benzonitrile are shown in Table 1. In acetonitrile and benzonitrile, the base electrolyte is 0.1 M tetraethylammonium perchlorate, and in aqueous solution, 0.1 M chloride or 0.1 M iodide. The polarographic ranges are +0.5 V to −2.1 V in benzonitrile and +0.5 V to −2.8 V in acetonitrile. All potentials are *versus* the aqueous saturated calomel electrode without correction for liquid junction potential. $E_{\frac{1}{4}}$ and $E_{\frac{1}{4}} - E_{\frac{1}{4}}$ values are corrected for iR drop across the cell.

TABLE 1

	Water	*Acetonitrile*		*Benzonitrile*	
	$E_{\frac{1}{2}}$ (V)	$E_{\frac{1}{2}}$ (V)	$E_{\frac{1}{2}}-E_{\frac{1}{4}}$ (mV)	$E_{\frac{1}{2}}$ (V)	$E_{\frac{1}{2}}-E_{\frac{1}{4}}$ (mV)
Eu^{III}	−0.67[9]	+0.19	−72	+0.18	−59
	−2.00	−1.67	−27	−1.68	−33
Yb^{III}	−1.41[9]	−0.58	−64	−0.63	−80
	−2.00[9]	−1.70	−85	−1.64	−126
Sm^{III}	−1.80[9]	−1.02	−67	−1.00	−58
	−1.96[9]	1.69	−33	−1.58	−79
Nd^{III}	−1.83[9]	−1.57	−21	−1.50	−175
Pr^{III}	−1.86[9]	−1.50	−33	−1.54	−170
Tm^{III}	−1.86	−1.50	−71	−1.52	−180

Discussion

The results in Table 1 show that the polarographic behaviour of rare-earth ions in benzonitrile is very similar to that in acetonitrile except that the reductions of neodymium(III), praseodymium(III), and thulium(III) are much less reversible in benzonitrile. Contrary to expectation, the differences in half-wave potential between the two reduction waves of europium(III), ytterbium(III) and samarium(III) are slightly less in benzonitrile than in acetonitrile, and it is therefore not surprising that there is no evidence for stepwise reductions of neodymium(III) and thulium(III). This decrease in stability of the divalent states, despite the lower solvating power of benzonitrile, is probably due to one or both of the following factors:

(a) An increase in ion pairing between the perchlorate ion and the rare-earth trivalent ions in benzonitrile compared with acetonitrile.

(b) An increase in the complexing power of water in benzonitrile compared with acetonitrile. A small concentration of water is introduced by using hydrated perchlorates.

These results do, however, constitute further evidence that the rare-earth divalent ions are more stable to oxidation in solvents of low solvating power than in aqueous solution.

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Polarography of inorganic substances in dimethylformamide

In a recent paper, McMASTERS and co-workers[2] have reported half-wave potentials and reversibility data for eleven inorganic species in dimethylformamide, and have summarised the results of earlier work on inorganic compounds in this solvent. Quite independently of McMASTERS, we have also been making a more thorough study of this solvent than has hitherto been done, and the results and discussions of our observations on twenty-six inorganic species in dimethylformamide are now reported.

Experimental

Dimethylformamide was purified in the following way: It was allowed to stand overnight over anhydrous potassium carbonate and then distilled *in vacuo* from the solid. It was then kept overnight over calcium hydride, refluxed for 3 h over this solid at atmospheric pressure, and distilled *in vacuo* from the solid. The first quarter of the distillate was rejected as it contained an amine impurity which complexed with certain transition-metal ions. The water content of the dimethylformamide was less than $3 \cdot 10^{-3}$ *M*, as determined by Karl Fischer titration.

Potassium, magnesium and barium perchlorates were obtained from B.D.H. Ltd. and dried in a vacuum oven at 100°. Other perchlorates were prepared by well-established methods and dried *in vacuo* at room temperature. The amalgams were also prepared by orthodox methods.

All solutions were prepared and added to the polarographic cell in a glove-box. The concentrations of all electroactive ions in the solutions studied were approx. $5 \cdot 10^{-4}$ *M*. The concentration of ferrocene was approx. $2 \cdot 10^{-4}$ *M*. The concentrations of the amalgams were approximately as follows: indium $5 \cdot 10^{-5}$ *M*; bismuth, and gallium $2 \cdot 10^{-4}$ *M*; thallium $4 \cdot 10^{-4}$ *M*; and cadmium, lead and zinc, 10^{-3} *M*.

All potentials are referred to the silver–silver chloride–saturated tetraethylammonium chloride reference electrode. $E_{\frac{1}{4}}$-, $E_{\frac{1}{2}}$- and $E_{\frac{3}{4}}$-values are corrected for potential drop across the cell.

Base electrolytes—0.1*M* solutions of sodium and tetraethylammonium perchlorate—were prepared by dissolving the respective salts in dimethylformamide. Sodium perchlorate was prepared from sodium carbonate and perchloric acid (both of analytical-reagent grade) recrystallised from water, and dried at 200°. Tetraethylammonium perchlorate was obtained from Eastman Kodak and dried in a vacuum oven at 60°.

Apparatus

A Sargent model XV d.c. recording polarograph was used.

A Meites-type H-cell was employed. The reference electrode was a sheet of silver (2 cm × 5 cm) coated with silver chloride and immersed in dimethylformamide saturated with silver chloride, tetraethylammonium chloride and methyl cellulose. The horizontal cross-arm contained a gel of 25% (w/v) tetraethylammonium perchlorate in dimethylformamide containing 5% (w/v) of methyl cellulose. The solution compartment was fitted with a sintered-glass dispersion tube for bubbling dry, oxygen-free nitrogen through the dimethylformamide solutions.

The cell was immersed in a bath of water, the temperature of which was thermostatically controlled at 25.0°. The resistance of the cell was 500 Ω and 750 Ω with

0.1 *M* sodium perchlorate and 0.1 *M* tetraethylammonium perchlorate in the solution compartment, respectively.

Results

Polarographic data for the inorganic species in dimethylformamide are given in Table 1.

The polarographic range using 0.1 *M* sodium perchlorate and 0.1 *M* tetraethyl-

TABLE 1

Species	*Base electrolyte (0.1 M)*	$E_{\frac{1}{2}}$ (V)	$E_{\frac{1}{4}}-E_{\frac{3}{4}}$ (mV)
Ferrocene*	$NaClO_4$	+0.88	−65[R]
Copper(II)	$NaClO_4$	+0.41	33[R]
Bismuth amalgam	$NaClO_4$	+0.38	−114
Indium amalgam	$NaClO_4$	−0.03	−32
Lead amalgam	$NaClO_4$	−0.03	−32[R]
Lead(II)	Et_4NClO_4	−0.03	40
Thallium amalgam	$NaClO_4$	−0.07	−63[R]
Thallium(I)	$NaClO_4$	−0.07	60[R]
Cadmium(II)	Et_4NClO_4	−0.17	33[R]
Cadmium amalgam	$NaClO_4$	−0.17	−28[R]
Gallium amalgam	$NaClO_4$	−0.37	−27
Cobalticinium ion	$NaClO_4$	−0.47	55[R]
Nickel(II)	$NaClO_4$	−0.53	64
Zinc(II)	Et_4NClO_4	−0.59	38
Zinc amalgam	$NaClO_4$	−0.59	−30[R]
Cobalt(II)	$NaClO_4$	−0.81	89
Manganese(II)	Et_4NClO_4	−1.12	34[R]
Barium(II)	Et_4NClO_4	−1.62	33[R]
Sodium(I)	Et_4NClO_4	−1.63	54[R]
Caesium(I)	Et_4NClO_4	−1.62	57[R]
Rubidium(I)	Et_4NClO_4	−1.65	55[R]
Potassium(I)	Et_4NClO_4	−1.67	54[R]
Strontium(II)	Et_4NClO_4	−1.80	44
Lithium(I)	Et_4NClO_4	−1.92	66[R]
Calcium(II)	Et_4NClO_4	−1.95	45
Magnesium(II)	Et_4NClO_4	−2.05	105

* Voltammetry with a rotating platinum electrode.
[R] Reversible wave. A wave was considered to be reversible if $E_{\frac{1}{4}}-E_{\frac{3}{4}}$ lay within $\pm(56 \pm 14)/n$ mV.

ammonium perchlorate as base electrolytes was + 0.8 V to −1.5 V and + 0.8 V to −2.4 V *vs.* the reference electrode, respectively. The voltammetric range using 0.1 *M* sodium perchlorate as base electrolyte was + 2.1 to −1.5 V *vs.* the reference electrode.

Discussion

These polarographic data were required by the authors for the compilation of a detailed list of formal electrode potentials in 0.1 *M* perchlorate solutions of various non-aqueous solvents, to aid them in their selection of the best solvents for the stabilisation of ions of unusual lower oxidation states such as indium(I) and thulium(II). This work will be reported later, but, in the meanwhile, it is felt that the data obtained may be of interest to analytical and physical chemists. LE GUILLANTON[1] has stated that the non-aqueous solvents most widely used for the polarographic analysis of organic compounds are acetonitrile and dimethylformamide.

Where a comparison of polarographic results can be made, our results are in reasonable agreement with those of McMASTERS *et al.*[2] and BROWN AND AL-URFALI[3], except that McMASTERS obtained two reduction waves for copper(II) while BROWN and we obtained one two-electron reduction wave. The presence of a trace of complexing agent such as chloride, which is known to form stable complexes with transition-metals ions in dimethylformamide[4], could explain the second copper(II) wave on McMASTERS' polarogram. The order of the oxidations and reductions is similar to that for aqueous solutions.

The application of dropping amalgam electrodes in dimethylformamide has supplied useful information, the oxidation waves for lead, thallium, cadmium and zinc amalgams being reversible in 0.1 *M* sodium perchlorate base electrolyte. Dropping amalgam electrodes should be of particular value for obtaining formal electrode potentials in solvents of low solvating ability, where the polarographic reduction of hydrated perchlorates is to be avoided if possible, since water is a complexing agent in such solvents.

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The Reduction of Some Inorganic Oxyspecies in Acetonitrile

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(*Submitted 7th August*, 1967)

SUMMARY

Since the proton is involved in the reduction of many inorganic oxyspecies in aqueous solution, it is to be expected that the reduction products of such species in aprotic solvents will be different from those in water. With this in view, polarographic studies have been made on eight oxyspecies in acetonitrile and controlled potential coulometric studies have been conducted on the vanadyl ion. There is good evidence that the reduction of vanadyl, permanganate and perrhenate ions in acetonitrile produce the ion VO^+ and vanadium(II) oxide, manganate ion and rhenate ion respectively.

INTRODUCTION

In aqueous solution, the reduction mechanism of many oxyspecies involves the hydrogen ion. Therefore, in the absence of protons in aprotic solvents, the reduction of these species must take place by a different mechanism and the products will almost always be different from those in aqueous solution.

Perhaps the most widely studied species of this type is oxygen itself. Results have been published[1–3] which show that in aprotic solvents, oxygen is reduced via the superoxide ion to peroxide in two one-electon steps.

$$O_2 + e \rightarrow O_2^-$$

$$O_2^- + e + 2M^+ \rightarrow M_2O_2$$

In aqueous solution the reduction of oxygen takes place in two two-electron steps. The products are hydrogen peroxide and either water or hydroxyl ions, depending on the pH of the solution.

It has been shown[5] that in dimethylsulphoxide, carbon dioxide is reduced in the following way:

$$2CO_2 + 2e \rightarrow CO + CO_3^=$$

while in aqueous, acidic solution the product is reported to be formic acid.[4]

The polarographic reductions of sulphur dioxide, nitrogen dioxide, nitrous oxide, nitric oxide and dinitrogen trioxide in dimethylsulphoxide have also been studied,[6,7] but the reduction products are not known.

In dimethylsulphoxide,[8] the uranyl ion is reduced to the stable UO_2^+ ion, a species which disproportionates in aqueous solution.

With the exception of a report[9] that the reduction of the nitrate ion is catalysed by polyvalent cations in dimethylsulphoxide, as in aqueous solution,[10] the reduction of anions in aprotic solvents has not been studied, although the results of considerable work on the reduction of oxyanions in molten salts have been published.[11]

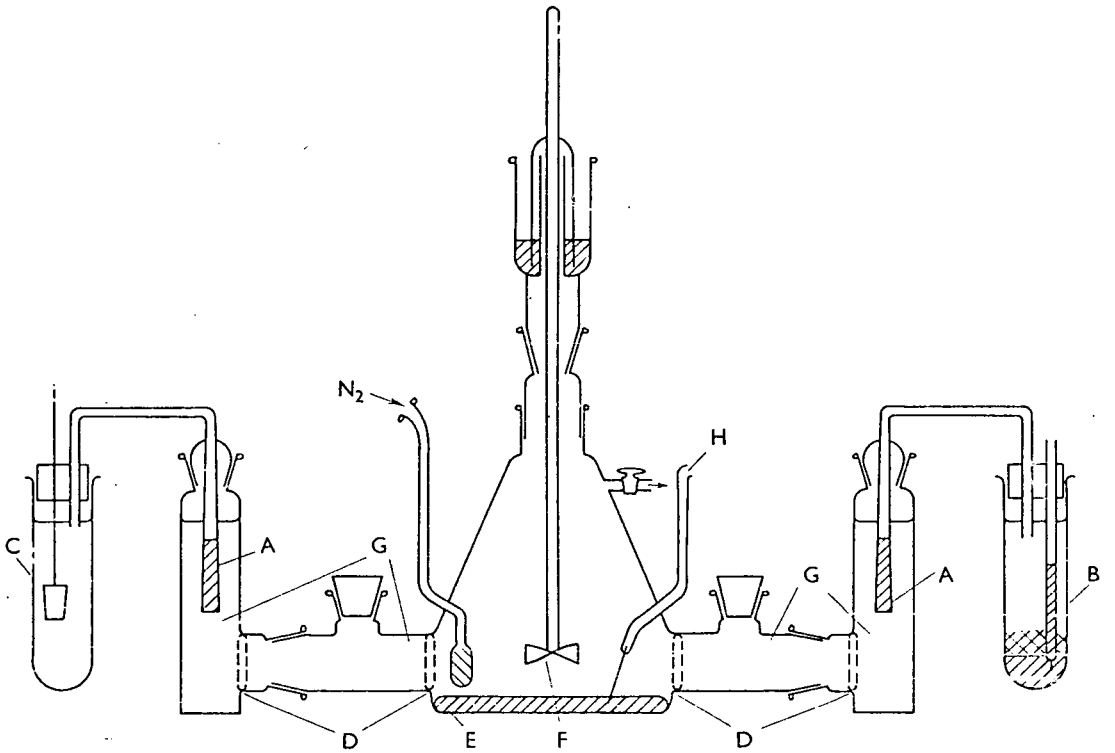
In this paper, the reduction of some oxyspecies in acetonitrile is discussed. Particular attention was paid to oxyspecies whose reduction products in acetonitrile were likely to be different from those in aqueous solution.

EXPERIMENTAL

A Sargent Model XV d.c. recording polarograph was used. The polarographic cell has been described elsewhere.[12]

A Southern Analytical A1680 potentiostat was used to supply a constant potential for the controlled coulometry. The current from the cell was passed through a standard resistance box and the potential drop across the box was recorded on a Sargent polarograph which could be used as a 2·5 mV recorder. The cell used for controlled potential coulometry is shown in Fig. 1.

The acetonitrile was B.D.H. reagent grade



A. Aqueous gel of 3·5% (w/v) agar in 0·1M $NaClO_4$.
B. Reference electrode—aqueous S.C.E.
C. Auxiliary electrode—Cu | saturated, aqueous Na_2SO_4.
D. Sinters, porosity No. 4.
E. Mercury pool working electrode.
F. Solution of electroactive species.
G. Base electrolyte solution.
H. Platinum contact to mercury pool electrode.

and was purified by the method of Olver and Forcier.[13]

The sulphur dioxide was supplied by B.D.H. Ltd. and the nitrogen dioxide by the Matheson Co. Inc. Both gases were used without further purification except for drying with phosphorus pentoxide.

Solutions of nitrate, chromate and perrhenate ions were prepared from their tetraethylammonium salts, which were made by standard techniques. Tetraethylammonium perchlorate was obtained from Eastman Kodak and dried at 60°C in a vacuum oven.

Vanadyl perchlorate was prepared by mixing aqueous solutions of vanadyl sulphate and barium perchlorate. The barium sulphate was centrifuged off and the water removed from the aqueous solution of vanadyl perchlorate under vacuum at room temperature. The crystals of vanadyl perchlorate which formed, were filtered off and redried under vacuum. The vanadyl content of the crystals was determined by a permanganate titration (vanadyl : found 19·54%, theoretical for $VO(ClO_4)_2.4H_2O$, 19·81%).

Uranyl perchlorate was prepared in a similar way from silver perchlorate and uranyl chloride. All other chemicals used were of the purest grades available.

All solutions were prepared and handled in a dry box, but electrochemical measurements were made with the cell immersed in a bath, thermostatted at 25°C. The solutions were degassed with a stream of oxygen-free, dry nitrogen.

All potentials are corrected for the iR drop across the cell and are quoted vs the aqueous S.C.E. without correction for the liquid junction potential between water and acetonitrile.

RESULTS AND DISCUSSION

Polarographic data are given in Table I for several species in acetonitrile. The base electrolyte was 0·1M tetraethylammonium perchlorate, with which the polarographic range was +0·5 V to −2·85 V. Selenium dioxide, iodine pentoxide and chromium trioxide were found to be too insoluble for reliable polarographic data.

TABLE I

Species	$E_{\frac{1}{2}}$ volts	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ mV
Nitrogen dioxide ..	>+0·5	—
Permanganate ..	>+0·5	—
Uranyl	+0·19	−60
	−0·04	−58
	−0·39	−65
Vanadyl	−0·60	−75
	−1·55	−440
Sulphur dioxide ..	−0·88	−71
Perrhenate	−2·58	−56
Nitrate	No reduction	—
Chromate	No reduction	—

Both permanganate and nitrogen dioxide react chemically with mercury. On shaking with mercury, a solution of nitrogen dioxide quickly changes colour from brown to blue, and then slowly becomes colourless while a white precipitate is produced. Addision and Logan[14] state that in an acetonitrile solution of nitrogen dioxide, the following equilibria exist:

$$NO_3^- + NO(CH_3CN)_n^+ \rightleftharpoons N_2O_4 + nCH_3CN \rightleftharpoons N_2O_4(CH_3CN)n$$

Thus the blue colour is probably due to the presence of dinitrogen trioxide, formed by the reaction of nitrogen dioxide with nitric oxide, produced by the reduction of the nitrosonium ion. The final precipitate contains a mercury nitrate.

The product of the reaction between mercury and acetonitrile solution of permanganate is a black precipitate. However, if a permanganate solution is shaken with sodium metal, the product is a green solution, presumably containing manganate ions. In an attempt to obtain a reduction wave for the permanganate ion, a voltammogram was run using a rotating platinum electrode, but no wave was obtained even at potentials as negative as −2·0 V versus the aqueous S.C.E. This must be due either to the reduction of permanganate being very irreversible at a platinum electrode or to the permanganate ion attacking the platinum to form a non-conducting layer on the surface of the electrode.

In view of the chemical reduction of permanganate and the polarographic data obtained for the perrhenate ion, it seems likely that perrhenate is reduced in a one-electron reversible step to the rhenate ion. However, because of the negative potential at which this reduction takes place, it is unlikely that the rhenate ion will be thermodynamically stable in acetonitrile. Certainly, when attempting to reduce the perrhenate ion chemically with potassium, the solvent was preferentially attacked.

It is probable that, as in aqueous solution, sulphur dioxide is reduced to the dithionite ion. It would be interesting to know whether the selenium analogue could be prepared by the reduction of selenium dioxide in aprotic solvents. However, selenium dioxide is not soluble in acetonitrile.

The three polarographic waves of approximately equal height obtained for the uranyl ion must be due to a mixture of complexes not in rapid equilibria. Although Gutmann *et al.*[8] report one reversible wave for the reduction of the uranyl ion in dimethylsulphoxide, they report that they also obtained three waves for the reduction of this species in dimethylformamide.

The polarogram of the vanadyl ion shows two waves of almost equal height. The first wave is well formed and diffusion controlled since its height is proportional to $h^{\frac{1}{2}}$ where h is the height of the mercury head, but the second wave is drawn out and extremely irreversible. Controlled potential electrolysis was carried out on 2×10^{-4}M solutions of vanadyl perchlorate at three potentials, −2·0 V, −0·75 V and −0·65 V vs the aqueous S.C.E. and the number of electrons, n, associated with the electrode reactions at these potentials are 1·98, 1·56 and 1·38 respectively. Since the polarogram shows two waves of equal height and n = 2 on the

plateau of the second wave, a value of n = 1 at the top of the first wave is to be expected. However, the second wave is extremely irreversible and the formal electrode potential for the reduction associated with this wave must be considerably more positive than the half-wave potential. Thus it is possible that the formal electrode potentials for the reductions associated with the two polarographic waves are close together, and under these circumstances, controlled potential coulometry at the top of the first wave will give n values greater than unity.

The current-time (i–t) data obtained by controlled potential electrolysis at −0·75 V were re-plotted as a graph of log i vs t. This graph was a curve which could be broken down into two straight lines. This indicates that two electrode reactions of different rates are proceeding simultaneously; that is, the addition of one electron to the vanadyl ion is a rapid process while the addition of a second electron is a much slower process.

The main product of electrolysis at −0·65 V is a green solution, while at −2·0 V the product is a mauve-brown solid. The initial solution of vanadyl perchlorate is, of course, blue. This further indicates that the reduction takes place in two one-electron steps, since vanadium(III) species are green in aqueous solution.

Therefore, the evidence is consistent with the following reduction path in acetonitrile:

$$VO^{++} + e \rightarrow VO^{+}$$

$$VO^{+} + e \rightarrow VO \downarrow$$

while in aqueous solution the vanadyl ion is almost always reduced directly to the divalent ion:

$$VO^{++} + 2H^{+} + 2e \rightarrow V^{++} + H_2O$$

However, the species VO^{+} seems to have only limited thermodynamic stability in acetonitrile and much of its stability is due to its reduction being kinetically hindered.

It seems likely that other novel oxyspecies could be prepared by electrolytic oxidation or reduction in aprotic solvents.

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Electrochemical Behaviour of Simple Cations

20

Half-wave potentials for the reduction of some simple cations in water and in non-aqueous solvents are shown in Table 13 *versus* the aq. S.C.E. without liquid junction potential. For these waves, $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ is less than or equal to $68/n$ mV, so that the waves are assumed to be reversible or almost so. Some could be quasireversible but this is unlikely since, in all cases where the oxidations of the metal amalgams have been investigated using dropping amalgam electrodes, $E_{\frac{3}{4}}$ (reduction) equalled $E_{\frac{1}{4}}$ (oxidation) for the appropriate couples. These values can therefore be taken as formal electrode potentials. The half-wave potentials were corrected for liquid junction potentials using the pilot ion method with thallous ion.

When these formal electrode potentials obtained in different solvents are compared, it is at once apparent that the potential of a couple usually becomes more positive as the coordinating ability of the solvent for the cation decreases. This is expected from theory (see below). The approximate order of coordinating ability of solvents for cations is dimethylsulphoxide > dimethylformamide > water > acetone > propylenecarbonate > acetonitrile > nitromethane > dichloromethane as has been ascertained from the heat of reaction of these solvents with acceptor molecules.[162, 163, 164] If the values for couples in Table 13 are compared the following order of potentials with sign reversed is obtained, dimethylsulphoxide > dimethylformamide ≏ water > propylene carbonate ≏ acetonitrile > acetic acid > sulpholane > nitromethane. Where applicable this closely follows the order of coordinating ability given above.

It must be stressed however that the formal electrode potentials in Table 13 are a measure of the free energy of solution of the gaseous ions in these

TABLE 13

Formal Electrode Potentials for Some Simple Ions in Water and in Non-aqueous Solvents

Solvent	Couples and formal electrode potentials (V *versus* aq. S.C.E.)								References
	$Tl^{II/0}$	$Pb^{II/0}$	$Cd^{II/0}$	$Zn^{II/0}$	$Mn^{II/0}$	$Ba^{II/0}$	$Yb^{III/II}$	$Sm^{III/II}$	
Dimethylsulphoxide	−0·46	−0·47	−0·62	−0·98		−1·99			158
[a] Water	−0·46	−0·38	−0·58	−1·00	−1·46	−1·94	−1·41	−1·80	—
[b] Dimethylformamide	−0·46	−0·42	−0·56	−0·98	−1·51	−2·01	—	−1·84	—
[c] Acetonitrile	−0·46		−0·45	−0·81	−1·27	−1·82	−0·76	−1·77	—
Propylene carbonate	−0·46	−0·31	−0·40			−1·90	−1·07		134
Acetic acid	−0·46	−0·29	−0·36						156
Sulpholane	−0·46	−0·27	−0·27		−1·16				135
Nitromethane	−0·46	−0·24	−0·25						134

[a] Half-wave potential data in non-complexing base electrolytes from Meites,[160] except for manganese in 0·1 M sodium perchlorate solution.[160a]. [b] Half-wave potential data from reference 129, except $Sm^{III/II}$ from reference 161. [c] Half-wave potential data from Coetzee *et al.*[5] except for $Ba^{II/0}$ from reference 161. Except dimethylsulphoxide (base electrolyte 0·1 M sodium nitrate for thallium (I), lead (II), cadmium (II) and zinc (II)), water (note [a]) and acetic acid (base electrolyte 1 M lithium perchlorate), the solutions were 0·1 M in perchlorate which is non-complexing, except perhaps in solvents of very low coordinating ability.

solvents plus base electrolytes. Unlike standard electrode potentials, they do not reflect directly changes in the free energies of solvation of the cations. This is evident from a study of the thermodynamic cycle in Fig. 25.

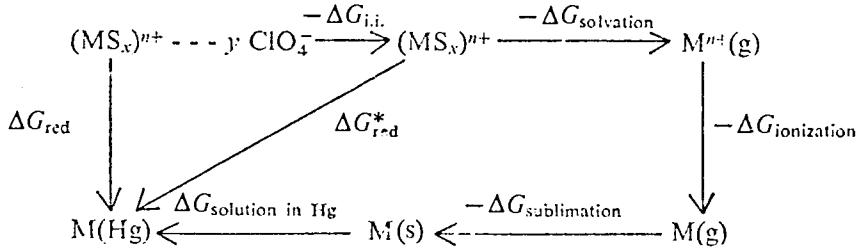

FIG. 25. Thermodynamic cycle for the reduction of ions in a solvent. $\Delta G_{i.i.}$ = free energy change resulting from ionic interactions; $\Delta G_{solvation}$ = free energy of solvation of the gaseous cations; $\Delta G_{ionization}$ = free energy change associated with the ionization of the gaseous atoms; $\Delta G_{sublimation}$ = free energy of sublimation; $\Delta G_{solution\ in\ Hg}$ = free energy change associated with dissolving the metal in mercury; ΔG_{red} = free energy change associated with the reduction at a mercury cathode (finite ionic strength); ΔG^*_{red} = free energy change associated with the reduction at a mercury cathode (zero ionic strength).

The coordinating ability of a solvent for cations is best expressed by the free energy of solvation of the gaseous ions at 25°C. For a cation in two solvents A and B

$$\Delta G^*_{red}(A) - \Delta G^*_{red}(B) = [-\Delta G_{solvation}(A)] - [-\Delta G_{solvation}(B)].$$

But $\Delta G^*_{red} = -n\,FE^*$ where E^* is the absolute standard electrode potential. Hence

$$-nF[E^*(A) - E^*(B)] = [-\Delta G_{solvation}(A)] - [-\Delta G_{solvation}(B)].$$

If the coordinating ability of A is greater than B then

$$-\Delta G_{solvation}(A) > -\Delta G_{solvation}(B).$$

Hence $E^*(B) - E^*(A)$ is positive or $E^*(B) > E^*(A)$.

The absolute standard electrode potential of the couple $(MS_x)^{n+}/M(Hg)$ in solvent B is therefore more positive than in solvent A. The standard electrode potential of the couple *versus* any reference electrode is therefore more positive in solution B (less coordinating) than in solution A (more coordinating). As the coordinating ability of a solvent for cations decreases, that is as the free energy of solvation of the gaseous ions becomes less negative, the standard electrode potential of the M^{n+}/M^0 couple becomes more positive. Using similar thermodynamic cycles it can be shown that the standard electrode potentials for $M^{n+}/M^{(n-a)+}$ couples also become more positive as the coordinating ability of the solvent decreases ($a = 1, \ldots, n-1$).

It is the formal electrode potentials which are measured polarographically, and these become more positive as the free energies of solution of gaseous ions become less negative. The free energy of solution of gaseous ions is $\Delta G_{ionization} + \Delta G_{i.i.}$.

Frequently, but by no means always, a decrease in the coordinating ability of a solvent, that is a decrease in $-\Delta G_{\text{solvation}}$, is paralleled by a decrease in its dielectric constant and an increase in $-\Delta G_{\text{i.i.}}$. Hence there are two opposing free energy terms here. Usually the change in $\Delta G_{\text{i.i.}}$ on going from a more coordinating to a less coordinating solvent is considerably less than the change in $\Delta G_{\text{solvation}}$, and so the values of formal electrode potentials for couples, formed from at least one cation, become, like the values of standard electrode potentials, more positive as the coordinating ability of the solvent decreases.

The effect of the $\Delta G_{\text{i.i.}}$ term has, in the past, been frequently neglected and for many systems this is not justified. For aqueous solutions, $\Delta G_{\text{i.i.}}$ is small for non-complexing anions such as perchlorate (a few electron centivolts at the most) but it cannot be neglected for solutions of base electrolytes in solvents of much lower dielectric constant such as acetic acid ($\varepsilon = 6$).

Very few data are available on the differences between standard and formal electrode potentials for couples in non-aqueous solvents. However, for the *tris*-1,10-phenanthroline iron (III)/*tris*-1,10-phenanthroline iron (II) couple in acetonitrile, Kolthoff and Thomas [165] have found a difference of 0·08 V between the standard and formal (0·1 M perchlorate) electrode potentials, and these are large cations. For smaller doubly charged and triply charged cations the effects of ionic interactions will be appreciable in solvents of low dielectric constant.

Finally, it is important to remember that, by the pilot ion method, liquid junction potentials are only estimated and not determined exactly. The formal electrode potentials in Table 13 could well be in error by 100 mV, so that it is pointless to attach thermodynamic significance to differences of less than 100 mV in formal electrode potentials obtained in different solvents. However, when generous allowance is made for the shortcomings in the pilot ion method, there is no doubt that the formal electrode potentials of most cationic couples move to more positive potentials as the coordinating ability of the solvent for cations decreases.

Occasionally, however, the opposite happens. The formal electrode potentials of the $Cu^+/Cu(Hg)$ and $Ag^+/Ag(Hg)$ couples in acetonitrile, 0·1 M in tetraethylammonium perchlorate, are $-0{\cdot}52$ V and $+0{\cdot}23$ V *versus* the aq. S.C.E. without liquid junction potential, respectively (Tl^+ as pilot ion).[5] The standard electrode potentials of these couples in water are $+0{\cdot}15$ V [166] and $> +0{\cdot}4$ V [160] *versus* the aq. S.C.E. respectively. Acetonitrile complexes copper (I) and silver (I) ions more strongly than water does. These are termed specific effects, and they are rather uncommon.

The inorganic chemist is, of course, interested in putting these shifts in formal electrode potential to good use, possibly by synthesizing in solution ions of unusual oxidation state. Solvents, which coordinate more strongly

than water, are complexing agents in aqueous solution and complexing agents have been widely used to stabilize higher oxidation states in aqueous solution, for example the stabilization of silver (II) as the tetrapyridinesilver (II) ion. The use of non-aqueous solvents is, therefore, not always necessary for preparing ions in these unusual higher oxidation states; working in aqueous solutions with the complexing agent is often possible.

If the formal electrode potential for a couple in the presence of the complexing agent is more negative than +1·0 V *versus* the aq. S.C.E., then the oxidized form of the couple is likely to be stable in aqueous solution. However, if the formal electrode potential for a couple in the absence of a complexing agent is more positive than +2·0 V *versus* the aq. S.C.E., it is seldom possible to stabilize the oxidized form of the couple by adding a complexing agent sufficiently for it not to react with water, because few complexing agents are able to shift the formal electrode potential of a couple by more than one volt in a negative direction.

It should therefore be possible to stabilize some simple solvated ions of interesting higher oxidation states in non-aqueous solvents which coordinate cations more strongly than water and which themselves are more stable than water to oxidation. Species such as copper (III) and americium (IV) come to mind. Finding solvents which coordinate cations more strongly than water is no problem, but finding solvents that do this and are also stable to powerful oxidants, is more difficult. Liquid hydrogen fluoride is in this class.

Cations of unusual lower oxidation states are stabilized in solvents for which the free energy of solution of gaseous ions is less negative than in aqueous solution. For example, the formal electrode potentials of the samarium (III)/samarium (II) and samarium (II)/samarium amalgam couples in 0·1 M aqueous tetramethylammonium iodide are −1·80 V and about −1·96 V *versus* the aq. S.C.E. respectively,[160] and in acetonitrile, 0·1 M in tetraethylammonium perchlorate, are −1·17 V and about −1·88 V *versus* the aq. S.C.E. without liquid junction potential, respectively (Tl^+ as pilot ion).[5] The samarium (II) state has been appreciably stabilized to oxidation in acetonitrile.

It is interesting to speculate on the possibility of preparing in acetonitrile, or in other solvents of low coordinating ability, cations which disproportionate in aqueous solution. The two ions that immediately come to mind are copper (I) and indium (I) because reliable information on the formal electrode potentials of the couples involving these ions in aqueous solution is available. These are

Cu^{2+}/Cu^+	$E^0 = -0{\cdot}08$ V	*versus* the S.C.E.[166]
$Cu^+/Cu(Hg)$	$E^0_a = +0{\cdot}15$ V	*versus* the S.C.E.[166]
In^{3+}/In^+	$E^{0\prime} = -0{\cdot}66$ V	*versus* the S.C.E. (3 M $NaClO_4$)[167]
$In^+/In(Hg)$	$E^{0\prime}_a = -0{\cdot}15$ V	*versus* the S.C.E. (3 M $NaClO_4$)[167, 168]

Very approximately, the free energy of solution of gaseous cations, excluding the hydrogen ion, in a particular solvent is proportional to the square of the charge on the ion. This being so, the differences in the formal electrode potentials of couples in two solvents of different coordinating abilities decrease in the order $M^{3+}/M^{2+} > M^{3+}/M^{+} > M^{3+}/M^{0} \simeq M^{2+}/M^{+} > M^{2+}/M^{0} > /M^{+}/M^{0}$, provided that there are no specific effects. In Table 13 the differences in the $E^{0\prime}$ values for M^{3+}/M^{2+} couples in water and acetonitrile are certainly much greater than the differences in $E^{0\prime}$ values for M^{2+}/M^{0} couples.

In a solvent such as nitromethane, one would expect the formal electrode potential for the $In^{+}/In(Hg)$ couple to be slightly more positive than $-0{\cdot}15$ V *versus* the aq. S.C.E. without liquid junction potential, but the formal electrode potential of the In^{3+}/In^{+} couple to be much more positive than $-0{\cdot}66$ V. If the shifts in potentials in nitromethane are such that $E^{0\prime}$ $(In^{3+}/In^{+}) - E^{0\prime}$ $(In^{+}/In\,(Hg))$ is now greater than 0·2 V, then In (I) will be almost completely stable to disproportionation. In fact, Ashraf and Headridge [134] have prepared solutions of indium (I) in nitromethane by oxidizing indium amalgam to indium (I) with a deficiency of anhydrous silver perchlorate. From such solutions, white crystals of indium (I) perchlorate are readily prepared by pumping off the solvent.

In acetone, 0·1 M in tetraethylammonium perchlorate, the formal electrode potentials of the Cu^{2+}/Cu^{+} and $Cu^{+}/Cu(Hg)$ couples are $+0{\cdot}37$ V and $+0{\cdot}15$ V *versus* the aq. S.C.E. without liquid junction potential respectively (Rb^{+} as pilot ion).[136] Copper (I) ion is obviously quite stable to disproportionation in acetone.

It is queried whether other cations of lower oxidation state, hitherto unknown in solution, can be prepared in suitable non-aqueous solvents. Among the rare earths, solid compounds of europium (II), ytterbium (II), samarium (II), thulium (II) and neodymium (II) are known. The polarographic reduction of the foremost three in aqueous solution produces first the divalent ion and then the amalgam. All three amalgams, ytterbium (II) and samarium (II) are rapidly oxidized by water and cannot be isolated in aqueous solution. Polarographic reduction of thulium (III) and neodymium (III) in aqueous solution shows no evidence for the formation, even momentarily, of thulium (II) or neodymium (II). Since the positive shift in the formal electrode potential of a III/II couple is much greater than that for a II/O(Hg) couple on transfer of the ions from water to a solvent of lower coordinating ability, the polarographic reduction of thulium (III) and neodymium (III) in solvents of lower coordinating ability than water, might be expected to produce evidence for thulium (II) and neodymium (II) in such solvents. However in acetonitrile [5, 130] and benzonitrile [130] both thulium (III) and neodymium (III) produce but one three-electron reduction wave showing that thulium (II) and neodymium (II) will, in the presence of mercury, disproportionate to the trivalent ion and the amalgam even in these solvents.

However, the zero oxidation state of rare earth metals, like the alkali metals, is appreciably stabilized to oxidation by amalgam formation, and the disproportionation of thulium (II) and neodymium (II) in solution will be aided if mercury is added to the system. The best chance of producing these species in solution will be by the controlled potential oxidation of the corresponding metal in a solvent, which shows relatively low coordinating ability for cations and which is stable to powerful reducing agents. Treating the rare earth metal in such a solvent with a deficiency of a suitable oxidizing agent could also produce the desired divalent ion. By similar techniques, gallium (I) and americium (II) may possibly be prepared in non-aqueous solvents of lower coordinating ability than water.

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INORG. NUCL. CHEM. LETTERS Vol. 3, pp. 475-478, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE STABILISATION OF INDIUM (1) IN ACETONITRILE

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(Received 8 August 1967)

Although several indium (1) compounds have been prepared in the solid state, this oxidation state has not previously been reported to exist in solution in appreciable concentrations. Biedermann and Wallin[1] have determined potentiometrically, the following formal electrode potentials for the indium system in 3.0 M aqueous perchlorate.

$$In^{3+} + 3e \longrightarrow In \quad - 0.58 \text{ V vs. aq. S.C.E.}$$
$$In^{3+} + 2e \longrightarrow In^{+} \quad - 0.66 \text{ V vs. aq. S.C.E.}$$
$$In^{+} + e \longrightarrow In \quad - 0.42 \text{ V vs. aq. S.C.E.}$$

Clearly indium (1) has negligible stability in aqueous solution. However, calculations based on these potentials and the differences between the half wave potentials for the polarographic reduction of cations in water[2] and in acetonitrile[3], indicate that indium (1) will have some stability in acetonitrile.

The results of indium amalgam polaragraphy in acetonitrile are now presented and a solution of indium ions, of which 75% is indium (1), has been prepared by the oxidation of indium amalgam with silver (1) perchlorate.

Experimental

The purification of acetonitrile, the procedure for recording polarograms and the polarographic cell have been described elsewhere[4].

The indium amalgams were prepared and handled under dry nitrogen. Lithium perchlorate and silver perchlorate were dried at 200° and room temperature (in vacuo) respectively and were then anhydrous.

The indium (I) contents of the acetonitrile solutions were determined by pipetting a suitable aliquot of the solution into a measured excess of aqueous dichromate and determining the unreacted dichromate with standard iron (II) solution. The total indium contents of the solutions [In (I) + In (III)] were determined by oxidising the indium (I) to indium (III) with acidified hydrogen peroxide solution and titrating the indium (III) with the standard EDTA solution[5].

Results and Discussion

Polarograms for indium amalgam in lithium perchlorate base electrolytes showed two waves not completely separated from each other. Data for these waves are given in table 1.

TABLE 1

Oxidation	Base Electrolyte	$E_{\frac{1}{2}}$ (V vs. aq. S.C.E.)	$E_{d.e}/\log \frac{i}{i_d - i}$ (mv)
In (0) → In (I)	0.1 M $LiClO_4$	-0.07	59^R
In (I) → In (III)	0.1 M $LiClO_4$	+0.04	48^I
In (0) → In (I)	0.01 M $LiClO_4$	-0.05	56^R
In (I) → In (III)	0.01 M $LiClO_4$	+0.09	69^I

R = reversible oxidation I = irreversible oxidation

Since the polarographic waves for the oxidation In (0) → In (I) are reversible, the half wave potentials quoted for these waves are

formal electrode potentials for the In (0)/In (I) couple in these base electrolytes. However, the polarographic waves for the oxidation In (I) → In (III) are irreversible and the formal electrode potentials for this couple must be more negative than the values given in table 1 and are probably similar to the values for the In (0)/In (I) couple. If this is so, the oxidation of indium amalgam with a deficiency of a suitable oxidant will yield an equilibrium mixture of indium (I) and indium (III).

Anhydrous silver perchlorate was selected as the oxidant. 50 mls. of indium amalgam were shaken with 25 mls. of acetonitrile containing a quantity of silver perchlorate insufficient for the quantitative oxidation of all the indium to indium (I). The silver which deposited, was removed by centrifugation and the solution analysed for indium (I) and indium (III). The results are shown in table 2 and indicate that an equilibrium mixture of indium (I) and indium (III) was indeed produced. From these results, the equilibrium constant of the reaction

$$In^{3+} + 2\ In\ (Hg) \rightleftarrows 3\ In^{+} + 2\ Hg$$

was calculated. Molar concentrations were used in the calculation of the equilibrium constant, K.

TABLE 2

$AgClO_4$ initially M	In (Hg) initially M	In (Hg) at equil. M	In^{+} at equil. M	In^{+++} at equil. M	K (24° C.)
5.05×10^{-2}	9.8×10^{-2}	8.1×10^{-2}	2.55×10^{-2}	0.85×10^{-2}	0.30
5.65×10^{-2}	10^{-1}	8.2×10^{-2}	2.63×10^{-2}	0.94×10^{-2}	0.28

Thus in acetonitrile, a solution of indium ions containing approximately 75% indium (I) and 25% indium (III) has been prepared. Work is continuing

to find a solvent of lower solvating ability than acetonitrile, in which indium (I) will have no tendency to disproportionate.

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Preparation of Indium(I) Perchlorate, Tetrafluoroborate, and Hexafluorophosphate

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Indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate have been prepared by reaction between indium amalgam and sub-stoicheiometric quantities of the appropriate silver(I) salts in acetonitrile, followed by partial evaporation of the solutions. The identities of the salts have been established by quantitative determination of total indium, In^I, and the respective anions.

THE indium(I) ion is thermodynamically unstable to disproportionation in aqueous solution as is evident from the following formal electrode potentials obtained in 3 mol dm^{-3} aqueous perchlorate by Biedermann and Wallin.[1]

$$In^{3+} + 3e^- \longrightarrow In \qquad E_{3/0}' = -0.343 \text{ V} \quad (1)$$

$$In^{3+} + 2e^- \longrightarrow In^+ \qquad E_{3/1}' = -0.426 \text{ V} \quad (2)$$

$$In^+ + e^- \longrightarrow In \qquad E_{1/0}' = -0.178 \text{ V} \quad (3)$$

Indeed Thiel [2] showed that indium(I) chloride and bromide, prepared by solid-state reactions, readily dissolve in water with the formation of indium metal due to the disproportionation of In^I [equation (4)]. Taylor

$$3In^+ \xrightarrow{\text{water}} In^{3+} + 2In \qquad (4)$$

and Sykes [3] prepared aqueous solutions containing *ca.* 3×10^{-4} mol dm^{-3} In^I in 0.01 mol dm^{-3} perchloric acid. In such acid solutions, In^I is unstable being slowly oxidised to In^{III} by hydrogen ion.

For these reasons, simple indium(I) compounds hitherto

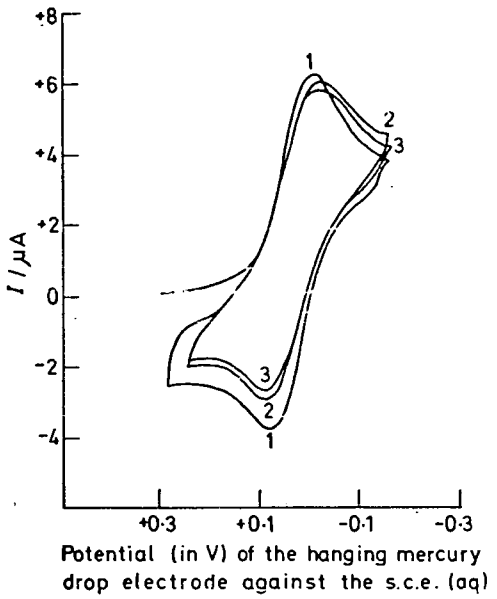
[1] G. Biedermann and T. Wallin, *Acta Chem. Scand.*, 1960, **14**, 594.

[2] A. Thiel, *Z. anorg. Chem.*, 1904, **40**, 280.

[3] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2419.

characterised have been prepared by solid-state reactions. These include the oxide, sulphide, selenide, telluride, fluoride, chloride, bromide, and iodide. It would be difficult to devise a solid-state reaction for the preparation of indium(I) compounds such as the perchlorate. However, such a compound should be readily prepared from a stable solution containing an appreciable concentration of indium(I) cations and low concentrations of indium(III) or other cations.

Headridge and Pletcher [4] predicted and then proved that In^{I} is more stable to disproportionation in acetonitrile than in aqueous solution. They prepared a solution containing 75% In^{I} and 25% In^{III} by reaction of silver(I) perchlorate (1.25 mmol) with indium amalgam



Cyclic voltammogram for indium(I) perchlorate in nitromethane. Scan rate, 0.04 V s^{-1}

(5 mmol of indium). Oxidation of In^{I} to In^{III} by hydrogen ions was not possible, because hydrogen ions were absent from the solution. Indium(I) ions should be even more stable to disproportionation in nitromethane than in acetonitrile because nitromethane has a lower co-ordinating ability for cations than has acetonitrile.[5] Hence it was logical to first attempt the preparation of indium(I) perchlorate from nitromethane solution. It was established that a solution containing In^{I} in nitromethane is readily prepared by shaking a 5×10^{-2} mol dm^{-3} solution of $Ag[ClO_4]$ in nitromethane (25 cm^3) with 0.1 mol dm^{-3} indium amalgam (50 cm^3). After the unchanged amalgam and silver had been removed by filtration in a glove-box under dry nitrogen, the presence of In^{I} was verified titrimetrically [4] and by cyclic voltammetry (Figure). Evidence for a reversible one-electron transfer reaction, $In^{I} \longrightarrow In^{0} \longrightarrow In^{I}$, is shown in the Figure. Sweeping the potential of the hanging mercury drop from +0.3 V *versus* the aqueous saturated calomel electrode (s.c.e.) to more positive potentials revealed an irreversible anodic peak for the oxidation of In^{I} to In^{III}. However, the concentration of In^{I} in nitromethane was only *ca.* 20% of the expected concentration and it was concluded that the solubility of indium(I) perchlorate is rather low in nitromethane, and that a better yield of solid compound would be obtained by repeating the preparation in acetonitrile but ensuring that very little In^{III} is produced together with In^{I} by stepping up the concentration of indium in the amalgam to 2 mol dm^{-3}.

The preparations of indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate are described in the Experimental section. For the determination of In^{I} in these compounds a slight modification of the titrimetric method used by Headridge and Pletcher [4] was employed. Total indium was determined by atomic-absorption spectrophotometry. All the three anions were determined spectrophotometrically after extraction as ion-association complexes with tris(1,10-phenanthroline)iron(II) into 1,2-dichloroethane. The method was a modification of that used for perchlorate by Fritz *et al.*[6] and for tetrafluoroborate [7] and hexafluorophosphate [8] by Archer *et al.*

RESULTS AND DISCUSSION

Indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate are hygroscopic and soluble in water. Successful preparation of these compounds was only possible when stringent precautions were taken to exclude water from the acetonitrile and from the nitrogen atmosphere of the glove-box where the preparations were made. Duplicate results for the analyses of the compounds are shown in the Table.

These results for the analysis of the three compounds

Composition of prepared samples of indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate

	Total indium content (%)		Indium(I) content (%)		Anion content (%)	
Indium(I) compound	found	calc.	found	calc.	found	calc.
Perchlorate	52.9 52.8	53.6	52.6 52.8	53.6	46.2 46.1	46.4
Tetrafluoroborate	56.5 56.3	56.9	56.3 56.1	56.9	42.5 42.8	43.1
Hexafluorophosphate	43.8 43.8	44.2	43.8 43.6	44.2	55.2 55.3	55.8

indicate that they are the compounds which we set out to prepare. The presence of silver and mercury in each compound was sought using atomic-absorption and molecular-absorption spectrophotometry based on the mercury(II)–dithizone complex [9] respectively, but in each

[4] J. B. Headridge and D. Pletcher, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 475.
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[7] V. S. Archer, F. G. Doolittle, and La V. M. Young, *Talanta*, 1968, **15**, 864.
[8] V. S. Archer and F. G. Doolittle, *Analyt. Chem.*, 1967, **39**, 371.
[9] E. B. Sandell, 'Colorimetric Determination of Traces of Metals,' 3rd edn., Interscience, New York, 1959, p. 629.

case these elements were absent. From the Table it can be seen that there was very little if any In^{III} in the three compounds, which are *ca.* 99% pure.

It may be possible to prepare other indium(I) compounds such as the acetate and nitrate using a similar procedure to that employed for the perchlorate, tetrafluoroborate, and hexafluorophosphate. The corresponding silver salts would have to be appreciably soluble in acetonitrile and the indium(I) salts would have to be at least sparingly soluble in acetonitrile. **CAUTION:** Care was always taken in handling the indium(I) perchlorate because it is potentially unstable (detonates, see Experimental section), a good reducing agent being present with an oxidising anion. Similar care would be necessary when working with indium(I) nitrate.

EXPERIMENTAL

Silver(I) perchlorate (B.D.H.) and tetrafluoroborate and hexafluorophosphate (Fluorochem Limited, Glossop) were dried overnight in a vacuum oven at room temperature before use. Acetonitrile was purified and dried using the second method of Walter and Ramaley.[10] All the operations described below in the preparation of the indium(I) solutions were carried out in dry apparatus in a glove-box under an atmosphere of dry nitrogen.

Preparations.—Indium(I) perchlorate. Indium amalgam (2 mol dm^{-3}, 50 cm^3) was shaken with a solution (50 cm^3) of 0.1 mol dm^{-3} $Ag[ClO_4]$ in anhydrous acetonitrile for 1 h in a stoppered conical flask. The mixture was transferred to a separating funnel and the indium amalgam removed. The finely divided silver was removed from the solution by triple filtration through dried Whatman No. 1 papers to produce a clear colourless solution. The volume of the solution was reduced to about one fifth by evaporation *in vacuo* and the solution was decanted from the solid which had separated. A pale yellow *product* remained. This was pumped to complete dryness and further dried in a vacuum oven at 90 °C overnight. The yield was *ca.* 200 mg. The preparation was repeated twice with similar yields, and the products were combined and thoroughly mixed to produce *ca.* 0.6 g of salt.

CAUTION: In the initial stages of this work a sample of 'indium(I) perchlorate' was prepared by complete evaporation of acetonitrile *in vacuo*. The flask containing the product was transferred to a dry glove-box and the crystals of solid material (*ca.* 0.5 g) were removed from the walls of the flask with a glass rod. When an attempt was made to powder the crystals with a glass rod, detonation occurred. It is suggested that no attempt should be made to scale up the described preparative procedure for indium(I) perchlorate.

Indium(I) tetrafluoroborate and hexafluorophosphate. The methods were the same as that used for perchlorate except that, after shaking for 1 h, the flask and contents were warmed on a hot plate within the glove-box to *ca.* 60 °C in the preparation of the tetrafluoroborate and to *ca.* 50 °C in the preparation of the hexafluorophosphate. The mixture was maintained at the elevated temperature for 15 min, left to cool to *ca.* 40 °C, and then shaken again for 10 min before transferring to the separating funnel. This modification in the method was required because of the low solubilities of indium(I) tetrafluoroborate and hexafluorophosphate in acetonitrile at room temperature. The total yield of the very pale yellow *tetrafluoroborate* and the white *hexafluorophosphate* was *ca.* 0.4 g in each case.

Analysis of the Products.—Total indium. The total indium contents of the three compounds were determined by atomic-absorption spectrophotometry using a Unicam SP 90 instrument, the indium resonance line at 303.9 nm, and an air–acetylene burner. Two samples of each compound (10—25 mg) were dispensed into a dry weighing bottle inside a dry glove-box and weighed accurately using a five-place semimicrobalance. Each sample was dissolved separately in 1 mol dm^{-3} HCl (10 cm^3) plus a drop of hydrogen peroxide solution (30% w/v) in graduated flasks (100 cm^3) and the solutions were diluted to the marks with 1 mol dm^{-3} HCl. The concentrations of indium in the solutions were determined with reference to a calibration graph for 0—150 μg cm^{-3} of In^{III} in 1 mol dm^{-3} HCl.

Indium(I). Two samples of each compound (8—20 mg) were dispensed inside the dry glove-box and weighed accurately using a five-place semimicrobalance. Each sample was added separately to conical flasks containing standard potassium dichromate solution (*ca.* 0.017 mol dm^{-3}, 10 cm^3) in excess of that required to oxidise In^I to In^{III}, plus 0.5 mol dm^{-3} H_2SO_4 (2 cm^3), the acid dichromate solution having been previously deoxygenated by passing oxygen-free nitrogen for 10 min. The flask was warmed to *ca.* 40 °C and allowed to cool to near room temperature while maintaining the stream of nitrogen over the surface of the solution. Standardised ammonium iron(II) sulphate solution (*ca.* 0.09 mol dm^{-3} in 0.5 mol dm^{-3} H_2SO_4, 15 cm^3) in excess of that required to reduce unchanged dichromate, was added together with distilled water (30 cm^3), 5 mol dm^{-3} orthophosphoric acid (6 cm^3), and three drops of barium *N*-phenylanaline-2-sulphonate indicator (0.2% w/v). The unchanged Fe^{II} was titrated with the standard solution of potassium dichromate.

Anions. The following method was used for the determination of tetrafluoroborate. Standard solutions of 10, 20, 30, 40, 50, and 60 μg cm^{-3} of tetrafluoroborate anion in 0.2 mol dm^{-3} potassium fluoride–0.2 mol dm^{-3} hydrofluoric acid (fluoride buffer solution) were prepared from sodium tetrafluoroborate dried in a vacuum oven at 60 °C overnight. To each solution (10 cm^3) in Polythene bottles were added freshly prepared 0.01 mol dm^{-3} tris(1,10-phenanthroline)-iron(II) sulphate solution (5 cm^3) and 1,2-dichloroethane (20 cm^3), and the solutions were shaken in the bottles for 5 min. They were then transferred to Polythene separating funnels, where the organic layers were separated. These organic solutions were transferred to centrifuge tubes, and centrifuged for 2 min to remove any of the aqueous phase still present. A suitable volume was taken from each organic solution for measuring the absorbances in 1-cm glass cells at 520 nm. From these results the calibration graph was drawn. Two samples of indium(I) tetrafluoroborate (*ca.* 20 mg) were dispensed inside the glove-box and weighed accurately using a five-place semimicrobalance. The samples were separately dissolved in volumes (250 cm^3) of fluoride buffer solution and the resulting solutions (10 cm^3) were treated in the same way as the standard solutions. The concentrations of these solutions were determined from the calibration graph.

The hexafluorophosphate content of the sample of indium(I) hexafluorophosphate was determined in duplicate using the same method and *ca.* 10 mg of salt. The standard

[10] M. Walter and L. Ramaley, *Analyt. Chem.*, 1973, **45**, 165.

solutions were prepared from sodium hexafluorophosphate which had been dried overnight in a vacuum oven at 60 °C. The perchlorate content of the sample of indium(I) perchlorate was determined in duplicate in a similar way using *ca.* 25 mg of salt in water (500 cm^3). It was not necessary to work in fluoride buffer solution because perchlorate is stable to hydrolysis. The standard solutions were prepared from AnalaR sodium perchlorate which had been dried overnight in a vacuum oven at 60 °C.

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Voltammetric oxidation of anthraquinones in acetonitrile and nitromethane

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It is well known that quinones are reduced polarographically and voltammetrically in aprotic solvents in one-electron steps to the singly and doubly charged anions.[1] Fodiman and Levin[2] have used such reduction waves in the polarographic determination of anthraquinone derivatives. It has recently been observed in our laboratory that anthraquinones, but not benzoquinones, naphthaquinones and phenanthraquinones, can also be oxidized voltammetrically in acetonitrile and nitromethane to the singly charged cations. The voltammetric oxidations of anthraquinones have, therefore, been studied in some detail to ascertain if these reactions can be of use to the analytical chemist. The results of these investigations are now reported.

EXPERIMENTAL

Apparatus

A Beckman Electroscan 30 was used for voltammetric investigations with a rotating platinum electrode and for cyclic voltammetry with a stationary platinum electrode. A cell similar to that already described was used.[3]

Reagents

The quinones were recrystallized before use when necessary. Acetonitrile was purified by the method of O'Donnell *et al.*[4] Nitromethane was purified by fractional freezing.[3] Tetraethylammonium perchlorate was dried in a vacuum oven at 60° before use.

Recording of voltammograms and cyclic voltammograms

These were obtained for anthraquinones in 0·1*M* solutions of tetraethylammonium perchlorate in acetonitrile or nitromethane at 25°. Voltammograms were recorded, a voltage scan-rate of 0·24 V/min and a platinum cylindrical microelectrode rotated at 600 rpm being used. Cyclic voltammograms were obtained by use of the same electrode, not rotated, and a scan-rate of 0·04 V/sec.

RESULTS

The voltammetric ranges were from +1·8 to −1·5 V *vs.* an aqueous S.C.E. and from +2·1 to −1·3 V *vs.* an aqueous S.C.E., in acetonitrile and nitromethane respectively. Voltammetric data for the oxidation of anthraquinones in acetonitrile and nitromethane are given in Table I. The solutions were approximately $5 \times 10^{-4}M$ in the quinone.

Benzoquinones, naphthaquinones and phenanthraquinones were not oxidized before the final rise in current caused by the oxidation of the electrode, the solvent or the perchlorate ion of the base electrolyte.

TABLE I.—VOLTAMMETRIC DATA FOR THE OXIDATION OF ANTHRAQUINONES

	Acetonitrile		Nitromethane	
	$E_{1/2}$, V *vs.* aq.S.C.E.	$E_{3/4} - E_{3/4}$ mV	$E_{1/2}$, V *vs.* aq.S.C.E.	$E_{3/4} - E_{1/4}$, mV
9,10-Anthraquinone	+1·21	56	+1·20	55
1-Amino-9,10-anthraquinone	+1·33	70	+1·30	75
1-Amino-4-hydroxy-9,10-ant hraquinone	+1·01	70	+0·96	80
1-Methylamino-9,10-anthraquinone	+1·16	80	+1·15	61
1,4-Dihydroxy-9,10-anthraquinone	+1·53	110	+1·52	125
1,2,4-Trihydroxy-9,10-anthraquinone	+1·26	100	+1·25	130
1,2,5,8-Tetrahydroxy-9,10-anthraquinone	+1·21	110	+1·22	100

The values of i_1^{ox}/i_1^{red} were 1·0, 1·1 and 1·3 for 1-amino-9,10-anthraquinone in acetonitrile, 1-amino-4-hydroxy-9,10-anthraquinone in nitromethane and 1,2,4-trihydroxy-9,10-anthraquinone in nitromethane respectively, where i_1^{ox} and i_1^{red} are the limiting currents on the plateaus of the oxidation and first reduction waves respectively.

For 1-amino-9,10-anthraquinone in nitromethane, the limiting current is directly proportional to concentration as expected. Over the range of (0·6–2·5) × $10^{-4}M$ a graph of limiting current *vs.* concentration was a straight line passing through the origin. The standard deviation of the error in limiting current was 0·11 μA (9 points), which corresponds to a relative standard deviation of 1·0% at a quinone concentration of 2·5 × $10^{-4}M$. The error in limiting current is expressed by i_1 (obs) − i_1 (calc), where the values of i_1 (calc) are points exactly on the straight-line calibration graph of limiting current against concentration.

DISCUSSION

Since the first reduction waves are quite definitely a result of a one-electron reduction, the values of i_1^{ox}/i_1^{red} indicate that the anthraquinones were oxidized to the singly charged quinone radical cations. Values in excess of unity result if the radical cation reacts rapidly with its environment to produce at least one species which is itself oxidized at potentials on the plateaus of the oxidation waves. Cyclic voltammograms of the anthraquinone solutions showed peaks of the expected shape on the oxidation half-cycles but no peaks on the reduction half-cycles, thus verifying that the singly charged quinone radical cations are unstable and react rapidly with their environment.

As with 1-amino-9,10-anthraquinone, it is likely that other anthraquinones will also produce straight line calibration graphs of limiting current *vs.* concentration.

The results of this study indicate that these voltammetric oxidation waves should be suitable for the determination of anthraquinones in the presence of other quinones. When reduction waves are used, benzoquinones, naphthaquinones and phenanthraquinones interfere in the determination of anthraquinones in aprotic solvent media.

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Summary—The voltammetric oxidation of seven anthraquinones to the singly-charged radical cations has been investigated in acetonitrile and nitromethane. The voltammetric waves can be used for the quantitative determination of anthraquinones. Benzoquinones, naphthaquinones and phenanthraquinones are not oxidized in these solvents.

Zusammenfassung—Die voltammetrische Oxidation von sieben Anthrachinonen zu den einfach geladenen Radikalkationen wurde in Acetonitril und Nitromethan untersucht. Die voltammetrischen Wellen können zur quantitativen Bestimmung von Anthrachinonen verwendet werden. Benzochinone, Naphthochinone und Phenanthrenchinone werden in diesen Lösungsmitteln nicht oxidiert.

Résumé—On a étudié l'oxydation voltammétrique de sept anthraquinones en cations radicaux chargés simplement, en acétonitrile et nitrométhane. On peut utiliser les vagues voltammétriques pour la détermination quantitative d'anthraquinones. Les benzoquinones, naphtoquinones et phénanthrènequinones ne sont pas oxydées dans ces solvants.

Section 3. Atomic spectroscopic analysis with particular reference to the determination of trace elements in metals

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The Spectrographic Determination of Nickel in Molten Steels

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A prerequisite for the direct spectrographic analysis of molten steels in industrial furnaces is the knowledge that good quality spectra can be obtained from molten steel surfaces, and that precise quantitative determinations can be made by using such spectra.

The emission-spectrographic determination of nickel from a molten steel surface at 1600° C under an argon atmosphere has, therefore, been investigated. When a condensed spark between a graphite electrode and the molten steel surface was used, spectra of good quality were produced. The standard deviations in the error for the determination of 0·7 to 1·8 per cent. of nickel in molten and solid steel samples, analysed under similar conditions, were 0·045 and 0·022 per cent., respectively.

THE routine analysis of molten steel is usually made by withdrawing a sample from the furnace, allowing it to solidify and, after suitable machining, subjecting it to emission-spectrographic analysis on a direct-reading instrument. This whole operation takes about 5 to 10 minutes, and, from an economic standpoint, it would be desirable to reduce the time required for an analysis. This could probably be done by carrying out an emission-spectrographic analysis on the molten steel directly, but a search of the chemical literature reveals that only a few studies have been made on the quality and possible analytical application of emission spectra from a molten steel surface, and most of these are of a preliminary nature.

Balandin and Mandel'shtam[1] investigated the possibility of determining the composition of molten steel in an arc furnace without sampling, and state that this method should be practicable. The electric arc of the furnace was used as an excitation source. In experiments on a laboratory scale, Shaevich and Shubina have determined silicon in molten pig-iron[2] and carbon in molten iron - carbon alloys[3] by using emission spectrography with relative standard deviations of about 5 per cent. With a pulsed laser source and a large Littrow spectrograph, Runge, Bonfiglio and Bryan[4] have obtained satisfactory calibration graphs for the determination of 9 to 24 per cent. of nickel and 13 to 25 per cent. of chromium in three samples of molten stainless steels. The preliminary studies on the spectrographic analysis of molten steels made by Hilger and Watts Ltd. and by the British Iron and Steel Research Association are reviewed by Scholes and Williams.[5]

As few results are given in the above papers on the precision of spectrographic methods of analysis of molten steels, the authors have investigated the spectrographic determination of 0·7 to 1·8 per cent. of nickel in five steels at room temperature and in the molten state at 1600° C. These results are now reported.

EXPERIMENTAL

A molten steel surface was produced by the induction melting of a 1·8-lb cylindrical sample of steel in a magnesia crucible. An inert atmosphere was maintained above the molten surface by passing argon into a Vitreosil hood positioned over the crucible. This refractory cover was constructed with three holes in it. Light from the molten surface was directed through one hole to a continuous optical pyrometer, which allowed the temperature to be kept constant at 1600° C. Visual inspection of a spark could be made through the second hole and the third hole permitted light to enter a large quartz spectrograph.

With the electrode gap set at 3·8 mm, 15-kV condensed sparks were struck between the molten surface and two graphite electrodes. Light from one of the sparks, after passing through a quartz lens, was deflected by a surface-aluminised mirror along the optical axis of the spectrograph. Before entering the spectrograph the light beam passed through another quartz lens, which produced a de-focused image of the spark on the slits.

The molten steel surface was half an inch below the top of the crucible and, when the solid samples were analysed at room temperature, a cylinder of steel was placed in the crucible so that its surface was the same distance below the crucible top; otherwise the apparatus was identical.

The spectra from the solid and molten samples were photographed on Kodak B10 plates over the range 2800 to 5000 Å. The exposure time for the solid samples was 3 minutes but, with the molten samples, the intensity of the spark was less and the exposure time was increased to 5 minutes.

The spectra of the five samples, and that from an iron spark in conjunction with a rotating stepped sector, were recorded on the same plate. After developing, fixing, washing and drying in the recommended manner, the optical densities of the nickel line at 3414·77 Å and the iron line at 3417·84 Å were recorded with a Joyce Loebl microdensitometer for each spectrum from the steel samples. The optical densities for each step of the iron line at 3440·61 Å on the spectrum from the iron spark were recorded, and the plate-calibration curve constructed. The log intensity ratios for the line pair nickel 3414·77 - iron 3417·84 Å for the five samples were obtained from the plate-calibration curve and plotted against nickel concentration to obtain a calibration graph. The same procedure was used for both solid and molten samples.

Results

The five steels and their nickel contents are shown below.

Steel	EN 351	EN 352	EN 353	EN 24	EN 354
Nickel content, per cent...	0·77	0·98	1·23	1·40	1·74

Analysed samples of these steels were a gift from the English Steel Corporation Ltd. The calibration graphs for both the solid and molten steel samples are shown in Fig. 1.

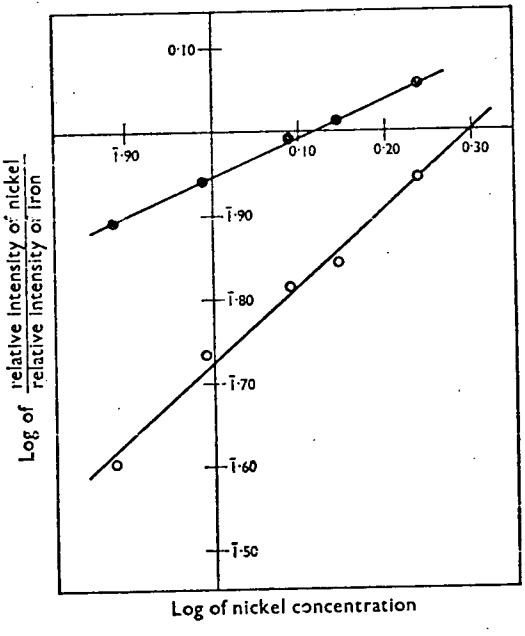

Fig. 1. Calibration graphs of log(relative intensity for nickel/(relative intensity for iron) against log (concentration of nickel): ● solid samples, ○ liquid samples

Discussion

It can be seen from Fig. 1 that the method is more sensitive for molten than for solid steel, as the slope of the calibration graph for the molten steels is the steeper of the two. When the results for the molten steels were re-plotted as intensity ratio against nickel concentration, a straight line passing through the origin was obtained. The standard deviation in the error in nickel concentration was 0·045 per cent., which corresponds to a relative standard deviation of 4·5 per cent. at a nickel concentration of 1 per cent. The standard deviation is based on five results, one for each of the five standards. The error in nickel concentration was expressed by c (observed) - c (calculated), where the values of c (calculated) were points exactly on the straight-line calibration graph of intensity ratio against nickel concentration.

A similar type of plot for the solid steels must also pass through the origin and give a curve concave to the nickel-concentration axis. This curvature probably resulted from self-absorption for the nickel line in the spectra from the solid samples. When a similar statistical treatment was made of this curve, the standard deviation in the error in nickel concentration was 0·022 per cent.

This study has shown that the spectrographic determination of nickel in molten steel is feasible and that the precision of the results is acceptable. The precision of the results for the molten steel samples could no doubt be improved if a satisfactory optical system could be devised to allow the exposure time to be appreciably reduced. There is every reason to believe that many other elements with low volatilities at 1600° C could be determined in molten steel by emission spectrography (Note). If this method were to be applied to the spectrographic analysis of molten steel in an industrial furnace, some way would have to be found for isolating a slag-free pool of molten steel under an argon atmosphere on the side of the furnace. This, however, is a problem for the mechanical engineer rather than the analytical chemist.

The authors are now hoping to obtain satisfactory calibration graphs for carbon in molten steels with similar apparatus and a vacuum spectrograph.

Note—The authors started their investigations by trying to obtain a suitable calibration graph for 0·4 to 1·7 per cent. of manganese in molten steel with a medium quartz spectrograph. Although a satisfactory calibration graph was obtained for manganese in five solid steel samples, consistent results for the determination of manganese in the molten samples could not be obtained. It was found that the concentration of manganese in the molten steels was, in fact, decreasing with time, for the vapour pressure of manganese above molten steel at 1600° C is appreciable, and the manganese vapour was being removed from the system by the argon stream.

We are indebted to Mr. Faine of this department and his workshop staff for building the electrode assembly. We gratefully acknowledge the receipt of grants for this work from the Science Research Council, English Steel Corporation Ltd., Firth-Brown Ltd., Guest, Keen and Nettlefold Steel Co. Ltd., Steel Company of Wales Ltd. and United Steel Companies Ltd.

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THE DETERMINATION OF TITANIUM IN ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY

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Although atomic absorption spectroscopy with an air–acetylene flame is a most versatile technique, it is not normally suitable for the determination of elements which form very stable oxide molecules in the flame, *e.g.* beryllium, aluminium, silicon, titanium, zirconium, vanadium, niobium, tantalum and tungsten. The stable oxide molecules can be dissociated by increasing the temperature of the flame and by arranging to have a fuel-rich flame in which reducing conditions are present. With this end in view, WILLIS AND AMOS[1,2] developed the nitrous oxide–acetylene flame for atomic absorption spectroscopy and obtained satisfactory sensitivities with this flame in the determination of beryllium, aluminium, silicon, titanium, vanadium and tungsten.

In the present paper, a method is described for the determination of titanium in steels, permanent magnet alloys and cast iron using the Hilger AA2 atomic absorption spectrophotometer and a nitrous oxide–acetylene flame. No preliminary separations are involved.

EXPERIMENTAL

Reagents

Hydrochloric, hydrofluoric and nitric acids, ammonia solution, methanol, ethanol and isopropanol were of analytical reagent grade.

Standard solutions of titanium, zirconium, niobium, tantalum and molybdenum. Titanium (1000 p.p.m.). 0.5 g of 'Specpure' titanium sponge was dissolved in hydrofluoric acid such that, on dilution to 500 ml, the concentration of acid was 1 *M*.

Zirconium (500 p.p.m.). 0.0676 g of 'Specpure' zirconium oxide was dissolved in concentrated hydrofluoric acid. The solution was evaporated just to dryness, the residue dissolved in 0.5 *M* hydrofluoric acid and the solution made up to 100 ml with this 0.5 *M* acid.

Niobium (500 p.p.m.). 0.0715 g of 'Specpure' niobium pentoxide was treated in the same way as for zirconium.

Tantalum (500 p.p.m.). 0.0611 g of 'Specpure' tantalum pentoxide was treated in the same way as for zirconium.

Molybdenum (500 p.p.m.). 0.0750 g of 'Specpure' molybdenum trioxide was dissolved in concentrated ammonia solution. The solution was evaporated to dryness, the residue dissolved in 0.5 *M* hydrofluoric acid, and the solution made up to 100 ml with this acid.

The standard solution of titanium was made up to exactly 500 ml in a graduated flask and immediately transferred to a dry polythene bottle. The other standard solutions were made up directly in polythene bottles.

Apparatus

Atomic absorption spectrophotometer. The Hilger AA2 instrument was employed with the following modifications. The standard burner for compressed air–acetylene was replaced by the burner described below. The upper inlet tube to the atomizer chamber was closed off, so that all the nitrous oxide used in the flame passed through the atomizer. Both the flow rates for nitrous oxide and acetylene were measured using the 2 compressed air rotameters on the standard rotameter holder. (The third rotameter for low flow rates of acetylene was not employed.) The open arm on the glass U-tube containing the water seal, which is connected to the atomizer chamber, was lengthened to 14 cm because of the relatively high pressure of nitrous oxide employed.

Hollow-cathode lamps. Lamps for titanium, zirconium, niobium, tantalum and molybdenum were obtained from Hilger and Watts Ltd.

Burner. The standard jet at the base of the burner in the acetylene lead-in tube was replaced by a jet of diameter 0.020″.

The burner head consisted of 2 bars of mild steel, each 6″ long, 5/8″ wide and 3/8″ deep, fitted together and bolted on to a brass chamber. Between the 2 bars, pieces of steel shim were inserted at each end to provide a slot of dimensions 2″ × 0.018″. The brass chamber was designed so as to produce a smooth transition for the gases from the pipe, onto which this brass chamber was placed, to the slot from which the gases emerged. The burner could be operated with or without water-cooling, but it was found that the increase in temperature on removal of the water-cooling, caused the paint on the walls of the burner housing to blister. A burner with water-cooling was, therefore, preferred. Water-cooling was achieved by circulating cold water through a copper pipe, fixed around the brass chamber, immediately below the bars of mild steel.

The procedure for obtaining the correct type of flame is as follows.

Connect the nitrous oxide and compressed air supplies to one of the air rotameter tubes through a T-piece. Ignite an air–acetylene mixture at the burner with an air pressure of about 20 p.s.i. Open the valve on the nitrous oxide cylinder and increase the pressure of nitrous oxide to about 25 p.s.i. Turn off the air supply and adjust the pressure of nitrous oxide to 30 p.s.i. Increase the acetylene pressure until a rose-red cone, approximately 3/4″ in height, is obtained.

The pressure and flow rates used were as follows: for nitrous oxide, pressure 30 p.s.i., flow rate 6.25 l/min; and for acetylene, pressure 12 p.s.i., flow rate 3.8 l/min.

RESULTS AND DISCUSSION

Sensitivities for the determination of elements

These were determined by spraying 0.1 *M* solutions of hydrofluoric acid containing 100 p.p.m. of the metal into the nitrous oxide–acetylene flame, and by assuming that flame absorbance is directly proportional to concentration, at least to a good approximation, over the concentration range of 0–100 p.p.m. The sensitivities are shown in Table I.

Hydrofluoric acid was chosen as solvent since it was desirable to develop a method suitable for many types of alloys. Niobium, tungsten, etc. are very conveniently held in solution in the presence of dilute solutions of this acid.

A considerable enhancement effect was found when aqueous alcoholic solutions of titanium were sprayed. The absorbances of aqueous ethanolic solutions were more than double those of the corresponding aqueous solutions; aqueous isopropanol solutions were less effective.

TABLE I

SENSITIVITIES FOR ELEMENTS WITH A NITROUS OXIDE–ACETYLENE FLAME

Element	*Wavelength (Å)*	*Sensitivity (p.p.m. giving 1% absorption)*	
		Aqueous solution	*Aqueous–organic solution*
Titanium	3643	6.5	2.0[a], 2.5[b], 3.5[c]
Zirconium	3601	27	13[d]
Niobium	3580	100	35[b]
Tantalum	2715	45	17[b]
Molybdenum	3133	1.5	0.7[b]

[a] 1 *M* aq. hydrofluoric acid–ethanol (1:9, v/v).
[b] 0.5 *M* aq. hydrofluoric acid–ethanol (1:4, v/v).
[c] 0.2 *M* aq. hydrofluoric acid–ethanol (1:1, v/v).
[d] 0.5 *M* aq. hydrofluoric acid–methanol (1:4, v/v).

Effect of other elements on the determination of titanium

Since it was intended to determine titanium in iron-base alloys the effect of a large excess of iron on the titanium absorption was first studied. The absorption for 50 p.p.m. of titanium in aqueous ethanol (1:1, v/v), which was 0.1 *M* in hydrofluoric acid, was enhanced by 15% in the presence of 5,000 p.p.m. of iron. This enhancement effect has also been reported by AMOS AND WILLIS[2]. A calibration graph for 0–50 p.p.m. of titanium in the presence of 5,000 p.p.m. of iron in the same aqueous ethanolic solution was a straight line passing through the origin. The slight scatter of the points about this straight line was subjected to statistical analysis, and it was concluded that 50 p.p.m. of titanium could be determined with a standard deviation of 0.5 p.p.m. The limit of detection for titanium is, therefore, considered to be 1 p.p.m.

Any interfering effects from other elements were ascertained by determining absorbances for 50 p.p.m. of titanium in aqueous ethanol (1:1, v/v), 0.1 *M* in hydrofluoric acid, when part of the 5,000 p.p.m. of iron was replaced by another element.

The absorbance for 50 p.p.m. of titanium + 5,000 p.p.m. of iron in the aqueous ethanolic hydrofluoric acid solution was 0.075, and interference was considered to have occurred when this figure changed by 0.001 or more absorbance units, on replacing part of the iron with the other element. There was no interference from 1,000 p.p.m. Cr + 4,000 p.p.m. Fe, 1,000 p.p.m. Co + 4,000 p.p.m. Fe, 1,000 p.p.m. Ni + 4,000 p.p.m. Fe, 500 p.p.m. Mn + 4,500 p.p.m. Fe, 250 p.p.m. Cu + 4,750 p.p.m. Fe, 250 p.p.m. Nb + 4,750 p.p.m. Fe, 250 p.p.m. W + 4,750 p.p.m. Fe, 100 p.p.m. Mo + 4,900 p.p.m. Fe, 100 p.p.m. V + 4,900 p.p.m. Fe, 50 p.p.m. S + 4,950 p.p.m. Fe, and 50 p.p.m. Ta + 4,950 p.p.m. Fe.

However, the absorbance was increased to 0.079 in the presence of 500 p.p.m.

Al + 4,500 p.p.m. Fe. There is a straight line relationship between the aluminium interference and the amount of aluminium, and 125 p.p.m. or more of aluminium interfere in the determination of titanium in aqueous ethanolic solution.

Analysis of steels, permanent magnet alloys and cast iron

For convenience, 0.5 g of alloy should be present in 100 ml of the final solution; this corresponds to 5,000 p.p.m. of metal in the final solution and 1% of titanium in the alloy then corresponds to 50 p.p.m. of titanium in solution.

Method. Dissolve 0.5 g of alloy in a Teflon beaker with 10 ml of concentrated hydrofluoric acid and 3 ml of concentrated nitric acid (Note 1). Evaporate the solution just to dryness and take up the residue in 10 ml of 1 *M* hydrofluoric acid and 10 ml of water. Warm to effect solution. Transfer the solution to a 100-ml graduated flask and rinse the beaker twice with 10-ml portions of water. Add 50 ml of ethanol to the flask and make up to the mark with water (Note 2). Transfer the solution at once to a dry polythene bottle. Spray this solution and then a standard solution containing 50 p.p.m. of titanium and 5000 p.p.m. of iron into the flame in the usual way, and determine the absorbances. Calculate the concentration of titanium in the solution by comparing the readings.

Note 1. With cast irons, dissolve the alloy in aqua regia, evaporate the solution to about 5 ml, add about 25 ml of 4 *M* hydrochloric acid, and filter off any undissolved carbon. Evaporate the filtrate just to dryness and take up the residue in 10 ml of 1 *M* hydrofluoric acid and 10 ml of water.

Note 2. In the case of permanent magnet alloys omit the ethanol, otherwise precipitation may occur. The calibration graph of flame optical density *versus* concentration is also a straight line through the origin for 0–50 p.p.m. of titanium in the presence of 5000 p.p.m. of iron in an ethanol-free solution, which is 0.1 *M* in hydrofluoric acid. However, with this solution, the method is not so sensitive for titanium. A solution of 50 p.p.m. of titanium + 5000 p.p.m. of iron gave a flame optical density of 0.037 compared with 0.075 in aqueous ethanol (1:1, v/v). In the absence of ethanol, however, there was no interference from 500 p.p.m. of aluminium + 4500 p.p.m. of iron, in place of 5000 p.p.m. of iron.

Iron(III) fluoride is only moderately soluble in hydrofluoric acid solutions and an alloy concentration of 5,000 p.p.m. was chosen for the development of a satisfac-

TABLE II

RESULTS FOR THE DETERMINATION OF TITANIUM IN ALLOYS USING ATOMIC ABSORPTION SPECTROSCOPY

Alloy	*Titanium content*	
	Cert. value (%)	*Found by A.A.S. (%)*
BCS 235/2 Ti stabilized '18-9' stainless steel	0.32	0.31, 0.32
BCS 335 austenitic stainless steel	0.46	0.46, 0.46
BCS 233 permanent magnet alloy	0.79	0.78, 0.80
BCS 312 permanent magnet alloy	1.19	1.20, 1.22
BCS 206/1 high Si and P cast iron	0.18	0.17, 0.18

tory method. However it is possible to obtain clear solutions with more concentrated solutions of many alloys, particularly in the absence of ethanol.

Results for the determination of titanium in 5 standard alloys are shown in Table II.

These results are considered to be satisfactory. It seems very likely that this atomic absorption spectroscopic method could also be applied to the determination of titanium in many other alloys. At no time was there any evidence of attack by the dilute hydrofluoric acid solutions on the glass atomizer chamber or the burner.

The authors acknowledge with thanks the loan of an AA2 atomic absorption spectrophotometer from Hilger and Watts Ltd. and are indebted to that company, and particularly to Mr. R. LOCKYER, for laboratory facilities for one of us (D.P.H.) during part of this work. They also thank the British Iron and Steel Research Association for a maintenance grant (for D.P.H.)

SUMMARY

A method is described for the determination of 0.1–1.2 % of titanium in steels, permanent magnet alloys and cast iron using atomic absorption spectroscopy with hydrofluoric acid solutions and a nitrous oxide–acetylene flame. No preliminary separations are required. When the correct conditions are employed there is no interference from the other elements commonly found in these alloys.

RÉSUMÉ

On décrit une méthode pour le dosage du titane (0.1–1.2%) dans les aciers, les alliages magnétiques et la fonte, par spectroscopie par absorption atomique. On utilise des solutions fluorhydriques et une flamme oxyde nitreux-acétylène. Il n'est pas nécessaire d'effectuer une séparation préliminaire. Lorsque les conditions sont correctes, les autres éléments généralement présents dans ces alliages ne gênent pas.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von 0.1–1.2% Titan in Legierungen mit der Flammenabsorptionsspektroskopie beschrieben unter Verwendung flussaurer Lösungen und einer Stickstoffoxid–Acetylen-Flamme. Vorhergehende Trennungen sind nicht erforderlich. Wenn die genauen Bedingungen eingehalten werden, gibt es keine Störungen durch andere Elemente, die im allgemeinen in diesen Legierungen vorkommen.

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LABP 19–39 ORIGINAL CONTRIBUTION

A comparison of electrodeless discharge tubes and hollow cathode lamps in atomic absorption spectroscopy

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Abstract

Electrodeless discharge tubes have been compared with hollow cathode lamps as light sources in atomic absorption spectroscopy. It has been found that absorption values are similar for the two light sources but that detection units are poorer for the electrodeless discharge tubes.

Comparaison de tubes de décharges sans électrodes et lampes cathodiques creuses dans la spectroscopie d'absorption atomique

Les tubes de décharge sans électrodes ont été comparés aux lampes cathodiques creuses comme sources de lumière dans la spectroscopie d'absorption atomique. Il a été trouvé que les valeurs d'absorption étaient similaires pour les deux sources de lumière mais que les éléments de détection étaient plus pauvres pour les tubes de décharge sans électrodes.

Vergleich von elektrodenlosen Entladungsröhren und Hohlkathodenlampen in der atomaren Absorptionsspektroskopie

Elektrodenlose Entladungsröhren sind mit Hohlkathodenlampen als Lichtquellen in der atomaren Absorptionsspektroskopie verglichen worden. Es ist gefunden worden, dass die Absorptionswerte für die beiden Lichtquellen ähnlich sind, aber dass die Nachweisseinheiten für die elektrodenlosen Entladungsröhren ärmer sind.

Since Dagnall and co-workers (1967) reported on the use of electrodeless discharge tubes in atomic absorption spectroscopy, conflicting views have been expressed about these tubes. Some workers have indicated that they can be used satisfactoriiy in place of hollow cathode lamps, but others have said that they are much less stable than hollow cathode lamps and cannot be recommended as light sources in atomic absorption spectroscopy. These two light sources have been recently compared in our laboratory and the results are shown below.

Apparatus

A Unicam SP 90 atomic absorption spectrophotometer was used along with Unicam hollow cathode lamps. The electrodeless discharge tubes were made using published methods (Dagnall *et al.* 1967; Marshall *et al.* 1967; Dagnall *et al.* 1968; Mansfield *et al.* 1968; Zacha *et al.* 1968; Browner *et al.* 1969). These tubes in 210L or 214L type cavities (Electro-Medical Supplies) were energized using an EMS Microtron 200 microwave unit fitted with an EMS voltage stabilizing transformer. For steady light output it was found necessary to shield a tube in a cavity from draughts by enclosing the cavity in a wooden box or, as suggested by Zacha *et al.* (1968), by enclosing the electrodeless discharge tube in a small vacuum jacket which itself fitted into a cavity. The electrodeless discharge tubes were operated at the lowest power for ignition because tubes operated at higher powers were noisier, although their light intensities were much greater. An electrodeless discharge tube was used in the position usually occupied by a hollow cathode lamp in the atomic absorption spectrophotometer. A warm-up time of 30 minutes was used with each hollow cathode lamp and electrodeless discharge tube.

The nitrous oxide-acetylene flame was operated in the usual way.

Comparison of relative light intensities, long term drifts and peak-to-peak noise for both sources

The relative light intensities were taken as the amplified photomultiplier outputs in millivolts for 0.1 mm slit. The long term drift is the upwards or downwards drift in light intensity per minute expressed as a percentage of the initial light intensity. These long term drifts were determined over 30 minutes. The peak-to-peak noise was measured from a recorder trace of expanded scale readings over a time interval of 80 seconds. It is expressed as a percentage of relative light intensity.

A comparison of the results obtained for hollow cathode lamps and electrodeless discharge tubes are shown in Table I. When a direct comparison is possible with aluminium, bismuth, cobalt, iron, nickel and titanium, it is evident that the long term drift of electrodeless discharge tubes is greater than with hollow cathode lamps but these tubes are sufficiently stable in this respect for use as light sources in atomic absorption spectroscopy. It will also be noted that the peak-to-peak noise for electrodeless discharge tubes is somewhat greater than that for hollow cathode lamps but not appreciably so. For 12 hollow cathode lamps the average peak-to-peak noise was 0.36 per cent of the light intensity. For 10 electrodeless discharge tubes it was 0.52 per cent of the light intensity. This will have an effect on the limit of detection for an atomic absorption spectrophotometric determination. If it is assumed that the peak-to-peak noises are similar after the light has passed through a flame (this is approximately so for most elements) and that the limit of detection corresponds to a concentration

TABLE I
Comparative data for hollow cathode lamps and electrodeless discharge tubes

Element	*Wavelength nm*	*Relative light intensity*		*Long term drift % R.L.I./min.*		*Peak-to-peak noise % R.L.I.*	
		H.C.L.	*E.D.T.**	*H.C.L.*	*E.D.T.*	*H.C.L.*	*E.D.T.*
Ag	328.1	2.24	—	0.016	—	0.68	—
Al	309.3	10.59	2.30 (210L)†	0.037	0.304	0.43	0.62
Bi	306.8	0.80	2.48 (214L)	0.035	0.054	0.61	0.60
Cd	228.8	—	3.80 (210L)	—	0.168	—	0.48
Co	240.7	1.20	2.48 (214L)	0.024	0.034	0.20	0.43
Cr	357.9	9.20	—	0.026	—	0.34	—
Fe	248.3	1.02	1.06 (214L)	0.057	0.115	0.27	0.40
Hg	253.7	—	9.00 (210L)	—	0.018	—	0.52
In	303.9	—	5.80 (214L)	—	0.057	—	0.59
Mg	285.2	2.58	—	0.027	—	0.22	—
Mn	279.5	0.80	—	0.062	—	0.27	—
Mo	313.3	4.02	—	0.029	—	0.22	—
Ni	232.0	1.58	1.01 (214L)	0.033	0.062	0.24	0.62
Ti	364.3	9.26	5.30 (214L)†	0.042	0.170	0.45	0.53
V	318.4	1.10	—	0.070	—	0.37	—
Zn	213.9	—	1.18 (210L)	—	0.021	—	0.45

*Type of cavity in parenthesis
†Without a vacuum jacket, otherwise with a vacuum jacket.

TABLE II
Comparison of analytical results for lamps and tubes

Element	*Wavelength nm*	*1% Absorption Value (μg/ml)*		*Detection Limit (μg/ml)*	
		H.C.L.	*E.D.T.*	*H.C.L.*	*E.D.T.*
Bi	306.8	1.0	0.9	0.6	0.7
Fe	248.3	0.5	0.5	0.14	0.25
Co	240.7	0.15	0.13	0.03	0.07
Ni	232.0	0.6	0.6	0.18	0.42
Ti	364.3	5.6	4.2*	1.5	2.9*

*Without vacuum jacket and with 0.08 mm slit; otherwise with a vacuum jacket and a 0.10 mm slit.

of metal which produces a signal equal to the peak-to-peak noise, then the limit of detection using hollow cathode lamps and electrodeless discharge tubes will on average be approximately one third and one half of the 1 per cent absorption values with the Unicam SP 90 instrument. For many determinations where the highest precision is not required, electrodeless discharge tubes are satisfactory as light sources and are much cheaper to make than hollow cathode lamps.

Comparison of 1% absorption values and limits of detection for both sources

Some 1 per cent absoption values and detection limits obtained with both sources using a nitrous oxide-acetylene flame are shown in Table II. As expected the 1 per cent absorption values are similar but the detection-limits are poorer for the electrodeless discharge tubes.

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The Determination of Trace Amounts of Calcium in Stainless Steels by Solvent Extraction Followed by Atomic-absorption Spectrophotometry

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A method is described for the atomic-absorption spectrophotometric determination of 2 to 60 μg g^{-1} of calcium in stainless steels after solvent extraction of most of the iron, chromium and nickel with acetylacetone and pyridine. For thirteen B.C.S. steels, the calcium contents varied from 4 to 51 μg g^{-1}. The standard deviation in the errors from the means for the various steels (fifty-eight determinations) was 1·4 μg g^{-1}. The results of applying the solvent-extraction procedure to twenty-five other elements of interest to the steelmaker are also reported.

The metallurgist is increasingly requiring information on the concentration of trace elements in stainless steel, as even minute traces of some elements can have detrimental effects on the desired properties of these alloys. In this paper a method is described for the determination of calcium in stainless steel at concentrations of 2 to 60 μg g^{-1}.

So that the interference of trace amounts of phosphate and silicate in the atomic-absorption spectrophotometric determination of calcium can readily be eliminated, a nitrous oxide - acetylene flame is used. With this flame the 1 per cent. absorption value for calcium is about 0·08 μg ml^{-1} for many commercial instruments in the presence of high concentrations of another ionisable metal. The standard deviation of the background "noise" is usually about one sixth of the 1 per cent. absorption value for cheaper atomic-absorption spectrophotometers. If the standard deviation of the sample "noise" is the same as the background "noise" (this is the minimum; it is usually appreciably greater), then the standard deviation in measured absorbance for a sample is twice the standard deviation in the background "noise," or about one quarter of the 1 per cent. absorption value. Therefore, under the best conditions, the standard deviation in the error for a calcium determination would be about 0·02 μg ml^{-1} with most British commercial instruments. For a 1 per cent. w/v solution of stainless steel this amounts to 2 μg g^{-1}; in practice, the figure is likely to be nearer 5 μg g^{-1}.

However, a precision approaching 1 μg g^{-1} was considered necessary for the determination of calcium in stainless steel and this could only be accomplished by using, in a direct method, a more concentrated solution of the steel, with the increased possibility of burner clogging, or by extracting the base elements from the steel into an organic solvent and concentrating the aqueous phase, which contained the calcium, before nebulisation. It was decided to adopt the latter method, for it has the additional advantage of allowing calibration graphs to be prepared from pure calcium solutions without the necessity of adding weighed amounts of Specpure base elements, which may contain calcium, to the standard solutions. This arises because the residual amounts of base elements, which are left in the aqueous phase after solvent extraction, have no interfering effect on the calcium signal.

A literature survey was undertaken to obtain information on suitable solvent-extraction methods for iron, chromium and nickel. Acetylacetone, which forms a separate layer with aqueous solutions, is a suitable extractant for iron(III) within the pH range of 1 to about 7.[1,2] The neutral tris(acetylacetonato)iron(III) is extracted. With nickel,[2] the maximum percentage extraction with 0·1 M acetylacetone in benzene occurs at pH 10 but only to the extent of 25 per cent. The low percentage extraction of nickel could result because most of the nickel may be present in the aqueous phase as $Ni(acac)_3^-$.

$$Ni^{2+} + 3Hacac \longrightarrow Ni(acac)_3^- + 3H^+.$$

Alternatively, the complex in the aqueous phase could be $[Ni(acac)_2(H_2O)_2]^0$, and hydrogen bonding between water molecules on the complex and those in the bulk of the solution would keep the neutral complex in the aqueous phase.

To induce the nickel to extract more completely into the acetylacetone layer, it is necessary to add a neutral non-hydrogen bonding complexing agent that will oust the third acetylacetonate anion or the water molecules and give the neutral complex, $[Ni(acac)_2L_2]^o$. Pyridine was selected for this purpose. From a buffer solution of equal amounts of pyridine and its hydrochloride at pH 5·2, the extraction of nickel was now almost complete (see below). Since this work was started, Tanino and Kitahara have also reported that nickel can be extracted from aqueous solution with chloroform containing acetylacetone and pyridine.[3]

Starý[1] states that chromium(III) is only extracted from aqueous solutions into pure acetylacetone if the chromium(III) solution is refluxed with acetylacetone. The dissociation of aquochromium(III) complexes before complex formation is very slow at room temperature, hence the necessity for refluxing. However, when acetylacetone *plus* pyridine were used with chromium(III) solutions that had been prepared by dissolving the metal in aqua regia and removing most of the acid by evaporation, it was found that 97 to 98 per cent. of the chromium was consistently extracted. This difference in behaviour of chromium(III) is under further investigation, but we have verified that no extraction of chromium(III) occurs at room temperature in the absence of pyridine.

The solvent-extraction procedure for the removal of most of the iron, chromium and nickel from stainless steels is described below. Calcium is not extracted at pH 5·2 by acetylacetone and pyridine and is left in the aqueous phase for subsequent determination by atomic-absorption spectrophotometry.

Experimental

Apparatus—

Atomic-absorption spectrophotometry was carried out on a Unicam SP90, fitted with a nitrous oxide - acetylene burner.

Reagents—

Hydrochloric acid, sp.gr. 1·18.
Nitric acid, sp.gr. 1·42.
Hydrofluoric acid, 40 *per cent. w/w.*
Potassium chloride.
Calcium carbonate.
These reagents were of analytical-reagent grade.

Iron, chromium, nickel, manganese and titanium metals and molybdenum trioxide were of Specpure quality (Johnson, Matthey Ltd.).

Acetylacetone—General-purpose reagent.
Pyridine—General-purpose reagent.
Re-distil both reagents before use.
Freshly distilled water—Store in a polypropylene aspirator.
Standard calcium solution A—Dissolve 0·624 g of dried calcium carbonate in the minimum amount of hydrochloric acid and dilute the solution to 1 litre in a graduated flask. Transfer the solution at once to a dry polythene bottle.

1 ml of solution A ≡ 250 μg of calcium.

Standard calcium solution B—Dilute 10 ml of solution A to 100 ml in a graduated flask. Transfer the solution at once to a dry polythene bottle.

1 ml of solution B ≡ 25 μg of calcium.

Preliminary investigations—

It was hoped to develop a satisfactory method for the determination of calcium by dissolving 1 g of stainless steel in aqua regia, evaporating the solution to the first appearance of solid, dissolving this solid in water, diluting the solution to 50 ml and extracting most of the iron(III) into an organic phase by shaking this solution with 50 ml of acetylacetone in a separating funnel. On adding 10 ml of pyridine and re-shaking the solution, it was then expected that most of the chromium(III) and nickel(II) would also be extracted into the organic phase, and calcium ions remain in the aqueous phase.

When acetylacetone reacts with metal ions to form complexes, hydrogen ions are released.

$$M^{3+} + 3Hacac \longrightarrow M(acac)_3 + 3H^+.$$

From 1 g of iron metal, 54 mmoles of hydrogen ions are produced. Another source of hydrogen ions in the solution is obviously the acid that remains in the solution when the steel solution has been evaporated to the first appearance of solid. It was established by titration with standard alkali that the 50 ml of steel solution, which were ready to be extracted with acetylacetone, always contained about 40 mmoles of hydrogen ions; 94 mmoles of hydrogen ions react with 7·6 ml of pyridine to produce pyridinium ions and, as excess of pyridine in the aqueous layer is necessary for complexation of the nickel, it was decided to use 10 ml of pyridine in the solvent-extraction procedure.

Therefore, the following tentative method was devised for preparing from stainless steel a solution suitable for nebulisation in the atomic-absorption spectrophotometer to determine the calcium content of the steel.

TENTATIVE METHOD—

Dissolve 1 g of steel in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid. Evaporate the resulting solution to the first appearance of appreciable solid material (about 7 ml). Take up the solid in water and dilute the solution to 50 ml. Transfer the solution to a separating funnel and shake the solution with 50 ml of acetylacetone. Add 10 ml of pyridine and re-shake the solution. Remove the lower aqueous layer containing the calcium ions and evaporate it to the first appearance of solid. Add 1 ml of potassium chloride solution (2·5 per cent. w/v in potassium ions) to suppress the ionisation of calcium atoms in the flame, take up the solid in water and dilute the solution to 25 ml in a graduated flask. Transfer the solution immediately to a dry polythene bottle.

The usual procedure for a blank solution is to replace 1 g of stainless steel by 1 g of Specpure iron and to carry through the procedure exactly as for a steel. However, it cannot be assumed that this iron is completely free from calcium, which is a trace impurity in most materials. Therefore, it was decided to dispense with the use of 1 g of Specpure iron and replace it with 54 mmoles of hydrogen ions, added as hydrochloric acid. (The calcium content of this acid is negligible.) The tentative procedure with the blank was, therefore, as follows.

TENTATIVE PROCEDURE WITH BLANK—

Evaporate 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid to 7 ml in a beaker. Add 10·8 ml of 5 M hydrochloric acid and dilute the solution to 50 ml. Transfer the solution to a separating funnel and proceed as for the steel solution.

Conditions had now been devised to test the effectiveness of the solvent-extraction procedure for iron, chromium and nickel. For convenience, the concentration of metal in the aqueous phase before extraction was taken as 0·2 per cent. w/v. The procedure was similar to that outlined above for steel except that 100 mg of Specpure metal were used. The concentration of metal ions left in the aqueous phase after solvent extraction was determined by atomic-absorption spectrophotometry. Standard solutions for the calibration graphs were prepared by adding suitable aliquots of more concentrated aqueous standard solutions to the aqueous phase of an extracted blank solution. The results obtained by solvent extraction with an atomic-absorption spectrophotometric finish are shown in Table I.

TABLE I

DATA ON THE SOLVENT EXTRACTION OF IRON, CHROMIUM AND NICKEL

Inorganic species	Wavelength, nm	Slit width, mm	Lamp current, mA	Percentage extracted
Iron(III)	248·3	0·10	15	98
Chromium(III)	357·9	0·08	10	97
Nickel(II)	232·0	0·10	15	95

The light path was 1 cm above the burner top, the acetylene flow-rate 3·0 l minute^{-1} at 15 p.s.i. pressure and the nitrous oxide flow-rate 5·0 l minute^{-1} at 30 p.s.i.

These results show that the iron, chromium and nickel are almost completely extracted with the tentative procedure.

It was hoped that it would be possible to prepare calibration graphs for calcium in stainless steels by adding aliquots of standard calcium solutions to the extracted blank solution together with the potassium chloride solution. However, before this method was adopted,

it was necessary to check that the low concentration of residual base elements had no effect on the calcium signal obtained in their absence, and that no calcium is removed into the organic phase in the extraction procedure.

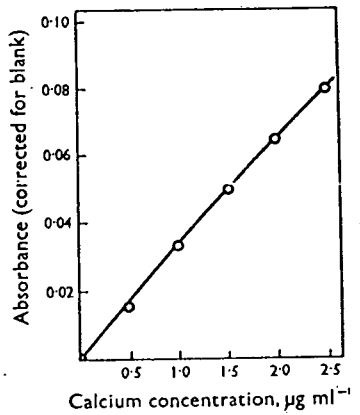

Fig. 1. Calcium calibration graph

A calibration graph obtained by adding aliquots of standard calcium solution to the extracted blank solution is shown in Fig. 1. An identical calibration graph was obtained when 20-mg amounts of iron(III) were added together with the aliquots of standard calcium solution. This proves that residual amounts of iron have no effect on the calcium signal, which is not unexpected, for the residual concentration of iron in the 25 ml of final solution is only 800 μg ml^{-1}, but the concentrations of potassium ion and pyridinium chloride are 1000 μg ml^{-1} and about 3·8 M, respectively.

Similarly a calibration graph obtained by adding aliquots of standard calcium solution to blank solutions before extraction, followed by the solvent-extraction procedure and work-up, was identical with that shown in Fig. 1. This proves that, as expected, no calcium is lost in the solvent-extraction step. In this instance the blank solution was prepared by using 1 g of Specpure iron per 50 ml of solution to be extracted rather than by adding 54 mmoles of hydrogen ions.

Finally, it was necessary to investigate the possible interference effects of other constituents of stainless steels on the calcium signals. This was carried out by replacing x g of the 1 g of iron by x g of the other element, where $100x$ per cent. is the maximum concentration of that element in stainless steels, adding aliquots of standard calcium solution, carrying through the solvent-extraction procedure and obtaining a calibration graph. The elements used with their respective concentrations are shown below.

Element	Chromium	Nickel	Molybdenum	Manganese	Titanium
Percentage present ..	30	25	3	2	1

These calibration graphs were identical with that obtained for extracted solutions of 1 g of Specpure iron *plus* added amounts of calcium. These results showed that residual amounts of other elements likely to be present in the aqueous phase of a steel solution, after solvent extraction, will have no effect on the calcium signals obtained in their absence. However, it should be pointed out that the above remarks have only been substantiated for amounts of calcium not in excess of 6 μg ml^{-1} in the solutions that are ready for spraying. This corresponds to a calcium concentration of 125 μg g^{-1} in a stainless steel. For larger amounts of calcium there may be interference effects.

The instrumental conditions for the atomic-absorption spectrophotometric determination of calcium are given later.

Main Study

A method was now available for the determination of calcium in stainless steels. However, two slight modifications to the tentative procedure were considered desirable. When the tentative procedure was applied to stainless steels, the final solution usually contained

a small precipitate of hydrated silica. As this precipitate could possibly contain a trace of a calcium silicate mineral that had remained undissolved on dissolution of the steel, it was decided to bring all of the constituents into solution at an early stage in the analysis. This was achieved by dissolving the steel with aqua regia in a Teflon beaker, evaporating the solution to about 7 ml, adding 3 drops (0·15 ml) of hydrofluoric acid solution (40 per cent. w/w) and simmering the solution for 15 minutes, with the beaker partly covered with a Teflon cover. When this procedure was adopted the final solutions were always clear.

Secondly, the volume of pyridine used in the solvent extraction was increased from 10 to 15 ml. With 15 ml of pyridine the concentrations of pyridine and pyridinium ion in the aqueous phase are about equal and the buffering capacity of the solution is at a maximum. With 10 ml of pyridine the ratio of pyridine to pyridinium ion is about 1 : 3.

The final method for the determination of calcium in stainless steels is, therefore, as follows.

Method

Dissolve 1 g of steel in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid in a 150-ml Teflon beaker. Evaporate the resulting solution to the first appearance of appreciable amounts of solid material (about 7 ml). Add 3 drops (0·15 ml) of hydrofluoric acid (40 per cent. w/w) and simmer the solution for 15 minutes, with the beaker partly covered with a Teflon cover. Take up the solid in water and dilute the solution to 50 ml. Transfer the solution to a Pyrex separating funnel and shake the solution with 50 ml of acetylacetone. Add 15 ml of pyridine and re-shake it. Remove the lower aqueous layer containing the calcium ions and evaporate it to the first appearance of solid. Add 1 ml of potassium chloride solution (2·5 per cent. w/v in potassium ions), take up the solid in water and dilute the solution to 25 ml in a Pyrex graduated flask. Transfer the solution immediately to a dry polythene bottle. Nebulise the solution in the Unicam SP90 atomic-absorption spectrophotometer by using the conditions given in Table II, and determine the absorbance for this solution.

Table II

Instrumental conditions for the determination of calcium

Acetylene flow-rate at 15 p.s.i., 1 minute^{-1}	3·1
Nitrous oxide flow-rate at 30 p.s.i., 1 minute^{-1}	5·0
Wavelength for use with the calcium lamp, nm	422·7
Slit width, mm	0·02
Lamp current, mA	12
Distance of centre of light path above burner, mm	10
Scale expansion	×3

Prepare the calibration graph for calcium in the following way. Evaporate in each of six 150-ml Teflon beakers, 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid to 7 ml. To each beaker add 3 drops (0·15 ml) of hydrofluoric acid (40 per cent. w/w) and simmer the solutions for 15 minutes, with the beakers partly covered with Teflon covers. To each solution add 10·8 ml of 5 M hydrochloric acid and dilute to 50 ml with distilled water. Transfer the solutions to separating funnels and shake with 50 ml of acetylacetone. Add 15 ml of pyridine and re-shake them. In all instances, remove the lower aqueous layers and evaporate them to volumes of about 10 ml. To six 25-ml graduated flasks marked 0, 0·5, 1·0, 1·5, 2·0 and 2·5 μg ml^{-1} of added calcium, add 0, 0·5, 1·0, 1·5, 2·0 and 2·5 ml, respectively, of standard calcium solution B. To each flask add 1 ml of potassium chloride solution (2·5 per cent. w/v in potassium ions). Then transfer the extracted and concentrated solutions to each flask. Wash out the beakers with distilled water, add the washings to the appropriate flasks and make up to the marks. The flask marked 0 μg ml^{-1} of added calcium is the blank solution for both the calibration graph and the steel solutions. It contains trace amounts of calcium from all of the reagents. Transfer the solutions immediately to dry polythene bottles. If a large Teflon beaker is available, a mixed acid stock solution, which has been extracted with acetylacetone and pyridine, can be prepared; 10-ml aliquots of this stock solution are then transferred by pipette into each 25-ml graduated flask. The solutions are now ready for nebulisation with the Unicam SP90 spectrophotometer.

The following spraying procedure should be adopted. With a ×3 scale expansion on the recorder, spray the 2·5 μg ml^{-1} calcium solution, then distilled water and finally the

0 μg ml^{-1} solution (the blank solution). Subtract the absorbance of the 0 μg ml^{-1} solution from that of the 2·5 μg ml^{-1} solution. The difference, which is the absorbance of the 2·5 μg ml^{-1} solution corrected for the blank, should be about 0·08. If so, the instrument settings are correct for a satisfactory determination of calcium. Now spray the solutions in the following order: (*i*), distilled water; (*ii*), 2·5 μg ml^{-1} calcium solution; (*iii*), distilled water; (*iv*), 2·0 μg ml^{-1} calcium solution; (*v*), distilled water; (*vi*), 2·5 μg ml^{-1} calcium solution; (*vii*), distilled water; (*viii*), 1·5 μg ml^{-1} calcium solution; (*ix*), distilled water; (*x*), 2·5 μg ml^{-1} calcium solution, and so on. Every second solution should be distilled water and every fourth solution the most concentrated standard solution. Continue in this way until all of the standard solutions, the blank solution and the steel solutions have been sprayed. The transmission of any solution containing calcium is determined by drawing the best lines through the "noise" on the recording for this solution and on the recordings for the distilled water immediately preceding and following that for the solution containing calcium, averaging the values for the distilled water and subtracting this average from the measured value for the solution containing calcium. This procedure corrects for slight drift in the base-line. The transmissions of every calcium-containing solution are converted into absorbances by using appropriate tables, and the absorbance of each solution is divided by the average absorbance for the two sprayings of the most concentrated standard solution that come immediately before and after it. This procedure corrects for any slight drift in flame temperature, rate of nebulisation, etc.

Construct the calibration graph by plotting these absorbance ratios against concentration of the calcium solution. Read off the concentration of calcium in the steel solution from this graph. The graph does not pass through the origin because there is some calcium in the blank solution. It will be appreciated that the same stock solutions of acids, etc., must be used in the construction of the calibration graph and in preparing the steel solutions. A new calibration graph is necessary only when fresh stock solutions have to be used.

Results

By using the above method the calcium contents of thirteen stainless steels were determined. These results are shown in Table III. The blank solution usually contained about 0·6 μg ml^{-1} of calcium. The absorbance for a solution containing 2·5 μg ml^{-1} of calcium was always about 0·08, after correction for the blank. This gives a 1 per cent. absorption value of 0·12(5) μg ml^{-1}.

Table III

Results for the determination of calcium in stainless steels

B.C.S. Steel	Calcium content, μg g^{-1}, by the described method
235/2	4, 4, 5, 8
246	7, 7, 10, 11
261	49, 51, 52, 52
331	3*, 4*, 4, 4, 5, 6
332	4, 6, 6, 6*, 7*, 8
333	2*, 2, 3, 5, 5, 5*
334	21, 22, 23, 23
335	12, 13, 14, 16
336	7, 9, 10, 11
337	6, 6, 7, 8
338	12, 12, 14, 16
339	10, 11, 12, 14
340	6, 6, 8, 11

* These results were obtained after subtracting a standard addition of calcium equivalent to 25 μg g^{-1} of calcium in the steel.

Solvent extraction of other elements with acetylacetone—

The percentages of iron, chromium, nickel and twenty-six other elements of interest to the steelmaker, which are extracted under the final conditions used for the analysis of stainless steels, are given in Table IV, together with information on related extraction procedures.

TABLE IV

EXTENT OF EXTRACTION OF VARIOUS ELEMENTS FROM THE AQUEOUS PHASE

Element	Extraction system and percentage extracted		
	I	II	III
Aluminium	96	96	96
Antimony(V)	0	0	0
Arsenic(V)	0	0	0
Bismuth	96	100	100
Boron	2	2	2
Calcium	0	0	0
Cerium(III)	90	90	91
Chromium(III)	98	98	99
Cobalt(II)	96	96	96
Copper(II)	97	98	98
Iron(III)	97	98	99
Lead	81	81	82
Magnesium	0	0	0
Manganese(II)	70	70	70
Molybdenum(VI)	53	85	87
Nickel	96	98	99
Niobium(V)	93	93	93
Phosphorus(V)	0	0	0
Selenium(VI)	1	1	1
Sulphur(VI)	0	0	0
Tantalum(V)	88	88	90
Tellurium(VI)	0	0	0
Thallium(I)	2	2	2
Tin(IV)	96	100	100
Titanium(IV)	6	8	8
Tungsten(VI)	2	0	0
Vanadium(V)	100	100	100
Zinc	87	92	91
Zirconium	91	92	92

In all instances, except for calcium, magnesium, iron, chromium and nickel, 50-ml aliquots of aqueous solution containing 50 mg or 0·5 mmoles of the element were used in the solvent-extraction procedure. With calcium, magnesium, iron, chromium and nickel, 250 μg, 250 μg, 1 g, 0·3 g and 0·2 g were used in 50 ml of solution, respectively. The 50-ml aliquots also contained 8·25 ml of concentrated hydrochloric acid and 2 drops (0·10 ml) of hydrofluoric acid solution (40 per cent. w/w). Separate aliquots were treated in the following way.

Procedure I—Shake the solution with 50 ml of acetylacetone, then add 15 ml of pyridine and re-shake it. (This is the procedure used in the analysis of the stainless steels.)

Procedure II—Carry out procedure I, remove the lower aqueous layer and re-shake it with 50 ml of acetylactone.

Procedure III—Carry out procedure I, remove the lower aqueous layer and re-shake it with 50 ml of chloroform - acetylacetone mixture (4 + 1 v/v).

In all instances the extracted aqueous layers were evaporated to the first appearance of solid. This solid was dissolved in a little water and the solution diluted to 25 ml. Aliquots of these solutions were analysed for element content by well established atomic-absorption spectrophotometric, solution spectrophotometric, titrimetric and gravimetric methods.

DISCUSSION

The results for the determination of calcium in stainless steels are considered to be very satisfactory. The standard deviation in the errors from the mean for the various steels is 1·4 $\mu g\ g^{-1}$. Less precise results for the determination of calcium in some of these stainless steels by two direct methods are available in a restricted report.[4] In nearly all instances our results are in good agreement with these results.

The results of the solvent-extraction studies (procedure I) indicate that a method similar to that used for calcium could probably be used for the determination of antimony, arsenic, magnesium, selenium, tellurium and thallium in steels. The 2 per cent. of thallium extracted can be attributed to aerial oxidation of a small amount of thallium(I) to thallium(III), which

is then extracted. This could be prevented by the presence of a suitable reducing agent. It will be noted in Table IV that re-shaking of the aqueous phase with more acetylacetone or with an acetylacetone - chloroform mixture results in more complete extraction with a few of the elements, but with most a second extraction makes little difference to the amount extracted by one shaking with acetylacetone and pyridine.

We thank the BISRA/Inter-Group Laboratories of the British Steel Corporation for a grant towards this work, and Mr. P. H. Scholes of BISRA and Dr. M. S. Taylor of Firth-Brown Ltd. for discussions on the project.

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Determination of Trace Amounts of Bismuth in Ferrous Alloys by Solvent Extraction Followed by Atomic-absorption Spectrophotometry

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A method is described for the atomic-absorption spectrophotometric determination of 2 to 130 $\mu g\ g^{-1}$ of bismuth in cast irons and stainless steels. From an aqueous solution of an alloy, 2·3 M in hydrochloric acid, 0·09 M in ascorbic acid and 0·2 M in potassium iodide, the bismuth was extracted quantitatively into isobutyl methyl ketone, by shaking the mixture once, while the base elements remained in the aqueous phase. After concentrating it, the organic phase was nebulised into an air - acetylene flame of a Unicam SP90 atomic-absorption spectrophotometer. The standard deviations in the errors from the means for various cast irons and stainless steels were 1·2 and 1·4 $\mu g\ g^{-1}$, respectively. The results of applying the solvent-extraction procedure to twenty-seven other elements of interest to the steelmaker are also reported.

Bismuth is an undesirable element in stainless steels as even 0·005 per cent. of bismuth reduces the hot ductibility of these steels.[1,2] A rapid and accurate method is therefore desirable for the determination of 0·0001 to 0·01 per cent. of bismuth in ferrous alloys. It was felt that a method with an atomic-absorption spectrophotometric finish might meet these requirements.

The best 1 per cent. absorption value for the determination of bismuth in aqueous solutions by atomic-absorption spectrophotometry with an air - acetylene flame is 0·7 $\mu g\ ml^{-1}$ for the 223·1 nm line.[3] However, with the bismuth hollow-cathode lamps used in our laboratory with the Unicam SP90 instrument, the light output at this wavelength was very low and excessively noisy. It was therefore necessary to use the much more intense bismuth line at 306·8 nm, even although this line was slightly noisy because it falls on the bandhead of the major hydroxyl band in the flame. By damping the output signal from the amplifier the noise was acceptable.

The 1 per cent. absorption value for the determination of bismuth in aqueous solutions in the air - acetylene flame of the Unicam SP90 is 2·0 $\mu g\ ml^{-1}$ with the 306·8 nm line. With 2 g of ferrous alloy in 100 ml of solution this sensitivity corresponds to a bismuth concentration in the alloy of 100 $\mu g\ g^{-1}$. Obviously a direct method is not sensitive enough for the determination of bismuth in the 0·0001 to 0·01 per cent. range. Therefore, it was necessary to use a simple extraction procedure that would enable the bismuth to be extracted from the base elements into an organic phase, which could then be concentrated before nebulisation into the flame of the atomic-absorption spectrophotometer.

Luke[4] has stated that traces of antimony, bismuth, cadmium, copper, indium and lead can be virtually quantitatively extracted from 5 per cent. w/v hydrochloric acid solution containing iodide by a double extraction with isobutyl methyl ketone. Ascorbic acid was added to solutions containing iron(III) to reduce it to iron(II) before adding the iodide. Iron(II), chromium(III) and nickel(II) were retained in the aqueous phase. We have found that by shaking the mixture once bismuth is quantitatively extracted into isobutyl methyl ketone from 2·3 M hydrochloric acid, which is 0·09 M in ascorbic acid and 0·2 M in potassium iodide. The base elements in ferrous alloys are again retained in the aqueous phase.

The basis of a suitable method for the determination of trace amounts of bismuth in ferrous alloys is thus established, as it was possible to concentrate the organic phase to a small volume by distilling off most of the solvent. The bismuth originally present in 2 g of alloy could readily be obtained in 5 ml of isobutyl methyl ketone. The 1 per cent. absorption value for the bismuth iodide complex in isobutyl methyl ketone, when sprayed into the air - acetylene flame of the Unicam SP90 spectrophotometer, was 0·7 μg ml^{-1} of bismuth. This corresponds to 1·8 μg g^{-1} of bismuth in a ferrous alloy, an appreciable improvement on the direct method.

A simple method is described below for the determination of 2 to 130 μg g^{-1} of bismuth in cast irons and stainless steels.

Experimental

Apparatus—

Atomic-absorption spectrophotometry was carried out on a Unicam SP90 spectrophotometer fitted with an air - acetylene burner.

Reagents—

Hydrochloric acid, sp.gr. 1·18.

Hydrochloric acid, 2·3 M—Dilute 1 litre of hydrochloric acid, sp.gr. 1·18, to 5 litres with distilled water.

Nitric acid, sp.gr. 1·42.

Hydrofluoric acid, 40 *per cent. w/w.*

L-*Ascorbic acid solution,* 16 *per cent. w/v*—Dissolve 40·0 g of L-ascorbic acid in a little warm 2·3 M hydrochloric acid and dilute the solution to 250 ml with the same acid.

Potassium iodide solution, 2 M—Dissolve 83·0 g of potassium iodide in 2·3 M hydrochloric acid and dilute to 250 ml with the same acid.

These reagents were of analytical-reagent grade.

Bismuth metal was 99·9995 per cent. pure (Koch-Light Laboratories Ltd.). Other metals and salts used were of analytical-reagent grade or Specpure quality (Johnson and Matthey Ltd.).

Isobutyl methyl ketone—General-purpose reagent. Re-distil before use.

Standard bismuth solution A—Dissolve 1·0000 g of bismuth metal powder in 5 ml of about 5 M hydrochloric acid containing 3 drops of concentrated nitric acid. Evaporate the solution nearly to dryness. Add 5 ml of concentrated hydrochloric acid and again evaporate nearly to dryness. Repeat this procedure. Dilute the solution to 1 litre in a graduated flask with 2·3 M hydrochloric acid. Dilute 10 ml of this solution to 100 ml in a graduated flask with 2·3 M hydrochloric acid.

1 ml of solution A $\equiv$ 100 μg of bismuth.

Standard bismuth solution B—Dilute 10 ml of solution A to 100 ml in a graduated flask with 2·3 M hydrochloric acid.

1 ml of solution B $\equiv$ 10 μg of bismuth.

Method

Determination of bismuth in ferrous alloys—

Accurately weigh and dissolve, with warming, 2 g of alloy in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid in a 150-ml Teflon beaker. Add 1 ml of concentrated hydrofluoric acid and simmer the solution gently for 5 minutes. Evaporate the solution nearly to dryness (Note 1). Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution nearly to dryness. Repeat this procedure. Dissolve the solids in warm 2·3 M hydrochloric acid and transfer the solution to a 250-ml graduated flask, washing the beaker with 2·3 M hydrochloric acid. Add 25 ml of ascorbic acid solution to the flask and mix the contents thoroughly, then add 25 ml of potassium iodide solution and dilute the solution to the mark with 2·3 M hydrochloric acid.

Transfer the contents of the flask to a 500-ml separating funnel, rinsing the flask with 5 ml of 2·3 M hydrochloric acid. Add 50 ml of isobutyl methyl ketone to the funnel and shake it vigorously for about 15 s. Allow the layers to separate and transfer the upper organic layer to a 100-ml pear-shaped distillation flask. By using an oil-bath at about 160° C distil

over the solvent until about 2 ml of solution remains in the flask. Transfer this solution to a dry 5-ml graduated flask, wash the distillation flask with a little isobutyl methyl ketone and make the solution in the graduated flask up to the mark with isobutyl methyl ketone.

Nebulise the organic solution containing extracted bismuth in the Unicam SP90 atomic-absorption spectrophotometer, by using the conditions given in Table I, and determine the flame absorbance of this solution with either the meter on the instrument or a recorder attached to it. In either event the output from the amplifier should be damped. The wash solution for the nebuliser is isobutyl methyl ketone (Note 2). Read off the concentration of the bismuth in the alloy from the calibration graph constructed as described below.

NOTES—

1. With cast irons, after the first evaporation nearly to dryness dissolve as much of the solids as possible in warm 2·3 M hydrochloric acid and filter the solution through a Whatman No. 541 paper to remove undissolved carbon. Collect the filtrate in a Teflon beaker and wash the filter-paper with 2·3 M hydrochloric acid. Evaporate the filtrate nearly to dryness, add the first of the 10-ml portions of concentrated hydrochloric acid and proceed with the method.

2. For a detailed account of the spraying procedure, an earlier publication by the authors should be consulted.[5]

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF BISMUTH

Acetylene flow-rate at 7 p.s.i., 1 minute^{-1}	0·9
Compressed air flow-rate at 30 p.s.i., 1 minute^{-1}	5·0
Wavelength for use with bismuth lamp, nm	306·8
Slit width, mm	0·10
Lamp current, mA	6
Distance of centre of light path above burner, mm	9

CALIBRATION GRAPHS—

For alloy samples containing 25 to 125 μg g^{-1} of bismuth weigh 2·00 g of Specpure iron into each of six 150-ml Teflon beakers and treat each sample in a manner identical with that described above for an alloy sample until the solutions are ready to be transferred to 250-ml graduated flasks. To each of six 250-ml graduated flasks add 0, 0·5, 1·0, 1·5, 2·0 and 2·5 ml of bismuth solution A. To each flask add the contents of a Teflon beaker and add the rinsings (2·3 M hydrochloric acid) of each beaker to the appropriate flask. Proceed with the addition of ascorbic acid and potassium iodide, the solvent extraction and the distillation as for an alloy solution but make the final isobutyl methyl ketone solutions up to the marks in 5-ml graduated flasks marked appropriately 0, 25, 50, 75, 100 and 125 μg g^{-1} of bismuth. The flask marked zero is the blank, both for the calibration graph and for the alloy solutions. Nebulise the solutions in the Unicam SP90 by using the conditions given in Table I and obtain a calibration graph by plotting absorbances of the bismuth solutions corrected for the blank *versus* concentration.

For alloy samples containing up to 25 μg g^{-1} of bismuth, the calibration graph is obtained in a similar way, except that 0, 1, 2, 3, 4 and 5-ml aliquots of bismuth solution B are used and the concentrations of bismuth in the final 5-ml volumes of isobutyl methyl ketone solution correspond to 0, 5, 10, 15, 20 and 25 μg g^{-1} of bismuth.

CHECK FOR INTERFERING ELEMENTS—

Only those elements which are extracted with the bismuth could interfere in the method. The extents to which twenty-seven other elements of interest to the steelmaker are extracted from the aqueous phase into the organic phase were therefore determined. Solutions of the metal or a suitable salt were prepared in 2·3 M hydrochloric acid and the composition of the aqueous phase adjusted before extraction to resemble as closely as possible that of a calibration solution but without the bismuth and iron. The concentrations of elements remaining in the aqueous phase were determined by well established atomic and solution absorption spectrophotometric, titrimetric and gravimetric methods. These results, as percentages extracted, are shown in Table II.

TABLE II

EXTENT OF EXTRACTION OF VARIOUS ELEMENTS AS IODIDE COMPLEXES INTO ISOBUTYL METHYL KETONE

Element	Percentage extracted	Initial concentration in aqueous phase, g per 250 ml	Element	Percentage extracted	Initial concentration in aqueous phase, g per 250 ml
Aluminium ..	0	0·05	Niobium	0	0·025
Antimony ..	94	0·01	Selenium ..	0*	0·01
Arsenic	56	0·01	Sulphur	0	0·01
Bismuth	100	0·05	Tantalum ..	0	0·01
Calcium	0	0·05	Tellurium ..	100†	0·01
Cerium	0	0·01	Thallium	Precipitate formed	0·01
Chromium ..	0	0·50			
Cobalt	0	0·50	Tin	9	0·01
Copper	94	0·01	Titanium ..	0	0·05
Lead	60	0·01	Tungsten ..	0	0·01
Iron	0	2·00	Silver	Precipitate formed	0·01
Magnesium ..	0	0·05			
Manganese ..	0	0·50	Vanadium ..	0	0·05
Molybdenum ..	43	0·02	Zinc	0	0·02
Nickel	0	0·50	Zirconium ..	0	0·01

* Cloudy aqueous phase. † Cloudy organic phase.

Only antimony, arsenic, copper, lead, molybdenum, tellurium and tin are extracted with bismuth from the aqueous phase and, with the exceptions of copper and molybdenum, these elements seldom occur in cast irons and steels in amounts greater than 0·5 per cent. Such alloys can contain up to 1 per cent. of copper and 5 per cent. of molybdenum. For each of the elements capable of being extracted, 250 ml of solution were prepared, which contained 1·4 g of iron, 0·4 g of chromium, 0·2 g of nickel, 100 μg of bismuth and 10 mg of the element except for copper (20 mg) and molybdenum (100 mg). The solutions were also 2·3 M in hydrochloric acid, 0·09 M in ascorbic acid and 0·2 M in potassium iodide. These solutions were treated by the above method and the amounts of bismuth in the 5-ml volumes of isobutyl methyl ketone determined from the calibration graph. In all instances the amount of bismuth thus determined was 100 μg. This showed that there was no interfering effect from any of the seven elements that are extracted wholly or in part with the bismuth.

RESULTS

Both calibration graphs were straight lines passing through the origin. At no time in this study did the blank solutions contain bismuth.

TABLE III

RESULTS FOR THE ANALYSIS OF SIMULATED SOLUTIONS OF STAINLESS STEELS

Base elements, per cent.			Bismuth content by addition, $\mu g\ g^{-1}$	Bismuth content found,* $\mu g\ g^{-1}$
Iron	Chromium	Nickel		
70	20	10	100	99, 99, 100, 100
70	20	10	50	50, 50, 50, 50
70	20	10	25	25, 25, 25, 25
70	20	10	5	5, 5, 5, 5
70	20	10	2·5	3, 2·5, 2·5, 2·5
60	30	10	100	101, 103, 101, 101
60	30	10	50	49, 49, 50, 51
60	30	10	25	26, 25, 26, 25
70	10	20	100	101, 99, 101, 102
70	10	20	50	50, 50, 50, 50
70	10	20	25	25, 25, 25, 25

* All of these results were obtained by using the recorder.

The results for the analysis of twelve solutions prepared to simulate 2-g samples of stainless steels are shown in Table III. The base elements were of Specpure quality. For

these "stainless steels" the standard deviation in the errors from the actual contents was 0·8 $\mu g\ g^{-1}$. The results for the analysis of four normal stainless steels are presented in Table IV. For these alloys the standard deviation in errors from the means was 1·4 $\mu g\ g^{-1}$. Finally, the results for the analysis of nine cast irons are presented in Table V. For these samples the standard deviation in the errors from the means was 1·2 $\mu g\ g^{-1}$.

TABLE IV

RESULTS FOR THE DETERMINATION OF BISMUTH IN NORMAL STAINLESS STEELS

Sample number	Nominal bismuth content, $\mu g\ g^{-1}$	Bismuth content found, $\mu g\ g^{-1}$
1	<10	7, 7, 5, 5, 5,* 5*
2	45	47, 47, 47, 47, 43,* 43*
3	60	62, 62, 63, 63, 66,* 64*
4	100	104, 103, 102, 103, 106,* 104,* 107*

* These results were obtained with the meter; others with the recorder.

TABLE V

RESULTS FOR THE DETERMINATION OF BISMUTH IN CAST IRONS

Sample	Bismuth content from B.C.I.R.A.,* $\mu g\ g^{-1}$	Bismuth content found,† $\mu g\ g^{-1}$
D1	85	83, 82, 81, 81
D2	130	132, 131, 130, 130
D3	16	15, 14, 15, 16
D4	65	62, 63, 61, 60
D5‡	180	186, 184, 184, 184
D6	85	82, 81, 86, 86
D7	19	20, 22, 22, 21
D8	63	60, 61, 59, 59
D9	90	90, 92, 92, 93

* These results were obtained by cathode-ray polarography after solvent extraction.[6]
† All of these results were obtained with the meter.
‡ The sample analysed consisted of 1 g of D5 *plus* 1 g of Specpure iron.

DISCUSSION

The above results are considered to be satisfactory. It seems likely that the method could also be used with slight modification for the determination of antimony in ferrous alloys.

It might be thought unnecessary to add iron to the bismuth solutions used in preparing the calibration graph, but when iron was absent the calibration graph for bismuth had a slightly steeper slope. A possible explanation is that dehydroascorbic acid produced by the reaction of ascorbic acid with iron(III) is partly extracted into the organic phase and has a slight depressive effect on the flame absorbance of bismuth solutions. For this reason the bismuth solutions, which are to be extracted, should also contain iron.

We thank the B.I.S.R.A./Inter-Group Laboratories of the British Steel Corporation for a grant towards this work, the B.I.S.R.A. Chemical Analysis Committee for the steels, and B.C.I.R.A. for the cast irons.

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LABP 20-34 ORIGINAL CONTRIBUTION

Determination of trace amounts of antimony in mild steels by solvent extraction followed by atomic absorption spectrophotometry

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Abstract

A method is described for the determination of 0-350 μg g⁻¹ of antimony in mild steels. The antimony was quantitatively extracted from an aqueous solution of the alloy into methyl iso-butyl ketone. After concentration of the organic phase, atomic absorption measurements were made using the air-acetylene flame of a Unicam SP 90 atomic absorption spectrophotometer. The standard deviation of the errors from the means was 2 μg g⁻¹ for antimony concentrations below 60 μg g⁻¹ and 4.6 μg g⁻¹ for concentrations in the range 175 – 350 μg g⁻¹.

Dosage des quantités d'antomoine entrant dans la composition des aciers doux grace à la méthode de l'extraction par solvant, suivie de la spectrophotométrie d'absorption atomique

L'auteur décrit une méthode permettant le dosage de 0-320 μg g⁻¹ d'antimoine dans les aciers doux. L'antimoine a été extrait quantitativement à partir d'une solution aqueuse de l'alliage dans de l'isobutyléétone de méthyle. Après concentration de la phase organique, on a effectué des mesures d'absorption atomique en utilisant un mélange d'air et d'acétylène enflammé fourni par l'Unicam SP 90 d'un spectrophotomètre d'absorption atomique. En règle générale, la déviation des erreurs par rapport aux moyennes a été de 2 μg g⁻¹ dans le cas de concentrations d'antimoine inférieures à 60 μg g⁻¹, et de 4.6 μg g⁻¹ dans le cas de concentrations allant de 175 à 350 μg g⁻¹.

Die Bestimmung von Antimonspuren in Weicheisen durch Lösungsmittelgewinnung, der eine atomische Absorptions-Spektrofotometrie folgt

Eine Methode für die Bestimmung von 0-320 μg g⁻¹ Antimon in Weicheisen wird beschrieben. Das Antimon wurde mengenmässig von der wässerigen Lösung der Legierung in das Methylisobutylketon entzogen. Nach Konzentrierung der organischen Phase wurden, mittels der Luft-Acetylenflamme eines Unicam SP 90 atomischen Absorptions-Spectrometers, atomische Absorptionsmessungen gemacht. Die Normalabweichung der Fehler vom Durchschnitt betrug 2 μg g⁻¹ für Antimonkonzentrationen unter 60 mg g⁻¹ und 4.6 μg g⁻¹ für Konzentrationen in dem Bereich von 175-350 μg g⁻¹.

Antimony is easily determined in the air-acetylene flame using the most sensitive resonance line at 217.6 nm. At this wavelength the 1 per cent absorption value for the determination of antimony in aqueous solution using the Unicam SP90 spectrophotometer is 2 μg ml⁻¹, which when applied to 2 g of ferrous alloy in 100 ml of solution is equivalent to 100 μg g⁻¹. Obviously a direct method is not sensitive enough for the determination of antimony in mild steels, where the content usually lies within the range of 10-150 μg g⁻¹, and a method involving solvent extraction followed by concentration of the organic phase prior to nebulisation is an attractive alternative.

Recent work carried out in this laboratory led to the development of a method for the determination of bismuth in ferrous alloys using atomic absorption spectrophotometry preceded by solvent extraction of the tetraiodobismuthate ion into methyl iso-butyl ketone (Headridge *et al.*, in press). From these investigations it appeared likely that with some modification the method could be useful for the determination of antimony in ferrous alloys.

Investigations showed that the extraction of antimony into methyl iso-butyl ketone, from hydrochloric acid solutions containing iodide, was quantitative in a single extraction at hydrochloric acid concentrations in the range 1.0 to 1.7 M. As antimony halides are known to be fairly volatile (Hillebrand *et al.*, 1953), experiments were carried out to investigate the loss of antimony in the initial dissolution and evaporation stages, and in the step involving distillation of the organic solvent. Results showed that under conditions similar to those used in the bismuth method no loss of antimony occurred.

It was evident that these observations formed a basis for a suitable method for the determination of antimony. The antimony was extracted from an aqueous solution containing hydrochloric acid 1.5 M, ascorbic acid 0.09 M and potassium iodide 0.2 M, into methyl iso-butyl ketone. After concentration of the organic phase the solution was subjected to atomic absorption spectrophotometric examination.

Experimental

Apparatus. Atomic absorption spectrophotometry was carried out using a Unicam SP90 spectrophotometer fitted with an air-acetylene burner. Resonance radiation was provided by an antimony electrodeless discharge tube powered by a Microtron 200 microwave generator fitted with a voltage stabilizing unit and frequency modulator unit operating at 50 Hz.

eagents

ydrochloric acid sp. gr. 1.18
itric acid sp. gr. 1.42
ydrofluoric acid 40 per cent w/w
scorbic acid
otassium iodide
otassium antimony tartrate, dried at 105°C.

All these reagents were of A.R. grade. Methyl iso-utyl ketone – General purpose reagent grade, redistilled efore use.

1.5. M hydrochloric acid – Dilute 650 ml hydrochloric cid sp. gr. 1.18 to 5 litres with distilled water.

Ascorbic acid solution, 16 per cent w/v – Dissolve 40 g -ascorbic acid in a little warm 1.5 M hydrochloric acid nd dilute to 250 ml with the same acid.

Potassium iodide solution, 2 M – Dissolve 83 g of otassium iodide in 1.5 M hydrochloric acid and dilute o 250 ml with the same acid.

Standard antimony solution – (a) *Solution A:* 500 μg ml^{-1} – Dissolve an accurately weighed sample of dry potassium antimony tartrate of known antimony content in warm 1.5 M hydrochloric acid, and dilute to 1 litre with the same acid so that the final solution contains 500 μg ml^{-1} of antimony.

The dry A.R. potassium antimony tartrate was 99.6 per cent pure assuming a formula of $KSbO\ C_4H_4O_6$. The antimony content was determined titrimetrically with standardised iodine solution (Vogel 1961).

(b) *Solution B:* 100 μg ml^{-1} – Dilute 20 ml of solution A to 100 ml in a graduated flask using 1.5 M hydrochloric acid.

Method for determination of antimony in ferrous alloys

Accurately weigh approximately 1 g of the steel and dissolve with warming in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid in a 150 ml Teflon beaker. Add 1 ml of hydrofluoric acid and simmer for 5 min before evaporating the solution almost to dryness. Add 10 ml concentrated hydrochloric acid and re-evaporate the solution almost to dryness. Repeat this procedure. Dissolve the residue in warm 1.5 M hydrochloric acid and transfer the solution together with washings of 1.5 M hydrochloric acid to a 250 ml graduated flask. Add 25 ml of the ascorbic acid solution and mix thoroughly before adding 25 ml of potassium iodide solution. Dilute to the mark with 1.5 M hydrochloric acid.

Transfer this solution to a 500 ml separating funnel, washing the flask with 1.5 M hydrochloric acid. Add 50 ml of methyl iso-butyl ketone and shake for 15 seconds. Allow the two layers to separate and transfer the organic layer to a 100 ml pear-shaped distillation flask. Distil over the organic solvent until a final volume of 2 ml remains by placing the distillation flask in an oil bath maintained at 150°C. Transfer the solution to a 5 ml graduated flask, wash the distillation flask with a little methyl iso-butyl ketone and finally dilute to the mark with methyl iso-butyl ketone.

Determine the flame absorbance of this solution using the Unicam SP90 spectrophotometer operating under the conditions listed in Table I.

Calibration graph. A calibration graph for the determination of antimony was prepared using six solutions prepared as described in the method above. These solutions each contained 1 g of specpure iron and 0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of antimony solution B respectively. The solution with no added antimony was the blank solution for both calibration and alloy solutions.

Interferences. The only elements which can interfere with the antimony determination are those which are also extracted. The only other elements found to be extracted were arsenic, bismuth, copper, lead, molybdenum, tellurium and tin (Headridge *et al.*, in press). Except for copper and molybdenum, which can occur in amounts up to approximately 1 per cent, none of these elements is likely to be present in mild steel in amounts greater than 0.1 per cent.

For each of these possible interfering elements, solutions were prepared containing 1 g specpure iron, 250 μg of antimony and 1 mg of interfering element. For copper a similar solution containing 10 mg of interfering element was prepared and for copper and molybdenum solutions containing 25 mg of interfering element were prepared. These solutions were subjected to the procedure described above. Flame absorbance values were obtained for all final solutions, and the antimony contents read from the calibration graph. In all but one case the amount of antimony found was 250 μg. In the solution containing 25 mg of copper a precipitate of copper iodide was formed and the recovery of antimony was incomplete. Some antimony was most likely lost by adsorption onto this precipitate. Solutions containing more than approximately 10 mg of copper formed such precipitates and thus suffered a loss of antimony. The method should not therefore be applied to steels containing more than 1 per cent of copper.

(*Continued on page 326*)

TABLE I

Instrumental conditions for atomic absorption spectrophotometric determination of antimony

Acetylene flow rate at 7 p.s.i.	0.8 l min^{-1}
Air flow rate at 30 p.s.i.	5.0 l min^{-1}
Wavelength of line used	217.6 nm
Slit Width	0.05 mm
Distance of centre of light path above burner	8 mm
Operation of Sb e.d.t. in 214L cavity, power	30 watts
modulation frequency	50 Hz

TABLE II

Sample	*Results by described method (%)*				*Average value (%)*	*Certificate value (%)*
BCS 325	0.0018	0.0022	0.0023	0.0018	0.0020	0.002
BCS 326	0.0056	0.0056	0.0056	0.0052	0.0055	0.005
BCS 327	0.0340	0.0340	0.0350	0.0346	0.0344	0.033
BCS 328	0.0254	0.0254	0.0247	0.0262	0.0254	0.026
BCS 329	0.0186	0.0176	0.0186	0.0176	0.0181	0.018
BCS 330	0.0176	0.0186	0.0181	0.0181	0.0181	0.018

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esults

he results for the analysis of six samples of mild steel ontaining antimony are shown in Table II.

As a wide concentration range was covered by the alibration graph, errors were calculated for two regions, ss than 60 $\mu g\ g^{-1}$ in steel and greater than 175 $\mu g\ g^{-1}$ in teel. For alloys containing less than 60 $\mu g\ g^{-1}$ the tandard deviation of the errors from the means was .0 $\mu g\ g^{-1}$, and for those alloys containing greater than 75 $\mu g\ g^{-1}$ of antimony the standard deviation of the rrors from the means was 4.6 $\mu g\ g^{-1}$.

Discussion

The results obtained for the analysis of these samples are onsidered to be satisfactory. For samples containing less han 100 $\mu g\ g^{-1}$ of antimony it should be possible to nprove the precision of the determination by using 2 g of sample for analysis.

Use of a hollow cathode lamp to provide resonance radiation should also result in better precision, because it has been shown (Headridge *et al.*, 1970), that detection limits are poorer when using electrodeless discharge tubes as radiation sources.

This method may also be suitable for the determination of antimony in stainless steels but some work will be necessary to investigate the effects, if any, of the large amounts of chromium and nickel on the antimony absorbance.

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The Determination of Tin in Steels by Solvent Extraction Followed by Atomic-absorption Spectrophotometry

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A method is described for the determination of 0·001 to 0·25 per cent. of tin in irons and steels. The tin from a 1-g sample of metal is extracted from an aqueous solution, which is 0·5 M in both hydrochloric acid and thiocyanate and 8 per cent. w/v in ascorbic acid, into isobutyl methyl ketone. The organic phase is concentrated to a small volume by evaporation and diluted to 10 ml. The tin content of this solution is determined by atomic-absorption spectrophotometry with a nitrous oxide - acetylene flame. Good results were obtained for the determination of tin in twelve B.C.S. irons and steels. The limit of detection was 0·001 per cent. of tin.

APPRECIABLE concentrations of tin have a detrimental effect on the hot-workability of carbon steels[1] and temper-brittleness can be caused by the presence of trace amounts of tin in alloy steels.[2] For these reasons the concentration of tin in steels is frequently determined. This concentration is usually within the range 0·005 to 0·1 per cent.

With the Unicam SP90, Series 1, atomic-absorption spectrophotometer, the concentration of tin that produced 1 per cent. absorption was 3·0 μg ml^{-1} in a nitrous oxide - acetylene flame when aqueous solutions and the 224·6-nm line were used. If an aqueous solution of a steel (1 per cent. w/v) was analysed by direct atomic-absorption spectrophotometry, the limit of detection for tin in the steel would be 0·03 per cent., assuming realistically that the limit of detection for aqueous solutions might be about the same as the concentration of tin that produces 1 per cent. absorption. Very recently, Thomerson and Price[3] reported that they were able to determine tin in steel down to about 0·01 per cent. by using a 2 per cent. w/v solution of the steel in perchloric acid and the Unicam SP90A, Series 2, atomic-absorption spectrophotometer. Clearly, with atomic-absorption spectrophotometers in the lower price range the direct method is not sensitive enough for the determination of tin in some cast irons and steels.

Headridge and Richardson[4] and Headridge and Smith[5] encountered a similar problem when determining bismuth and antimony, respectively, in steels and cast irons. The problem was overcome by extracting the trace element as an ion-association complex into isobutyl methyl ketone, evaporating the organic phase to small volume, diluting it to a definite volume and spraying the solution into the flame of an atomic-absorption spectrophotometer. It was felt that a similar approach might be adopted for the determination of tin in steels. The solvent-extraction procedure would have to be capable of separating the tin from large amounts of iron and, for alloy steels, of chromium and nickel.

Extraction of tin(IV) as a thiocyanate complex into isobutyl methyl ketone seemed to be a possibility, as tin(IV) is very effectively extracted into diethyl ether from an aqueous solution 0·5 M in hydrochloric acid and containing various concentrations of ammonium thiocyanate.[6] It was expected that iron(III) and molybdenum(V) would also be extracted into the isobutyl methyl ketone in high yield.[6] Most steels do not contain high concentrations of molybdenum, but for all steels the base element is iron. However, despite the fact that the formal electrode potential of the iron(III) - iron(II) couple will be lowered if a complex with thiocyanate is formed, it was felt that the iron(III) might be reduced to non-extractable iron(II) on the addition of excess of ascorbic acid. Preliminary experiments showed that this was so. Only 6 per cent. of the iron is extracted into isobutyl methyl ketone from an aqueous solution that is 0·5 M in hydrochloric acid, 0·5 M in potassium thiocyanate and 8 per cent. w/v in ascorbic acid, and, when the organic phase is shaken with an aqueous solution that contains only hydrochloric acid, potassium thiocyanate and ascorbic acid at these concentrations, almost all of the iron is stripped from the organic phase. In fact, only

0·3 per cent. of the iron originally present remained in the organic phase. A 1-g amount of iron was used in these preliminary extraction studies and the volumes used for all the aqueous and organic phases were 50 ml. Tin(IV) is quantitatively extracted from the aqueous phase in the first shaking with isobutyl methyl ketone and negligible amounts of tin are re-extracted into the aqueous phase in the second shaking.

A method based on the above extraction system is described in this paper for the determination in steels and irons of tin within the concentration range 0·001 to 0·25 per cent.

Experimental

Apparatus—

A Unicam SP90, Series 1, atomic-absorption spectrophotometer was used with a nitrous oxide - acetylene flame.

Reagents—

Analytical-reagent grade reagents were used unless otherwise stated.

Hydrochloric acid, sp. gr. 1·18.

Nitric acid, sp. gr. 1·42.

Ammonium and potassium thiocyanates.

Ascorbic acid solution—Dissolve 40 g of L-ascorbic acid in 250 ml of 0·5 M hydrochloric acid.

Ascorbic acid - potassium thiocyanate solution—Dissolve 40 g of L-ascorbic acid and 24 g of potassium thiocyanate in 500 ml of 0·5 M hydrochloric acid. This solution should be freshly prepared.

Iron metal—Specpure quality (Johnson Matthey Ltd.).

Formic acid, 98 to 100 per cent.—Fisons laboratory-reagent grade.

Isobutyl methyl ketone—General-purpose reagent. Redistil it before use.

Standard tin solution A—Dissolve 0·2500 g of granulated analytical-reagent grade tin metal in 8 ml of concentrated hydrochloric acid *plus* 2 ml of concentrated nitric acid in a 250-ml beaker. Add 1 ml of formic acid and heat the mixture gently until evolution of nitrogen dioxide ceases. Dilute the solution to 250 ml in a calibrated flask with 0·5 M hydrochloric acid.

1 ml of solution ≡ 1·000 mg of tin.

Standard tin solution B—Dilute 10 ml of standard tin solution A to 100 ml in a calibrated flask with 0·5 M hydrochloric acid.

1 ml of solution ≡ 0·1000 mg of tin.

Method

Determination of tin in ferrous alloys—

To 1·0000 g of iron or steel in a 100-ml beaker, add 12 ml of concentrated hydrochloric acid followed by 3 ml of concentrated nitric acid (Note 1). After reaction has ceased, add 5 ml of concentrated hydrochloric acid and heat the mixture gently for 10 minutes. Add 2 ml of formic acid and heat the mixture gently until evolution of nitrogen dioxide ceases. Evaporate the solution until solid first appears. Dissolve the residue in 25 ml of ascorbic acid solution and dilute the solution to approximately 50 ml with 0·5 M hydrochloric acid. Transfer the solution to a separating funnel, rinsing the beaker with a few millilitres of 0·5 M hydrochloric acid, add 2·4 g of potassium thiocyanate crystals (Note 2) and shake the funnel until the crystals dissolve. Add 50 ml of isobutyl methyl ketone and shake the funnel vigorously for 15 s. Run off the lower, aqueous phase and discard it. Add 50 ml of ascorbic acid - potassium thiocyanate solution to the remaining organic phase and shake the funnel vigorously for 2 minutes. Discard the aqueous phase.

Transfer the organic phase to a small distillation flask and distil over the isobutyl methyl ketone at an oil-bath temperature of 140 to 150 °C until a volume of approximately 7 ml remains in the flask (Note 3). Transfer the solution to a 10-ml calibrated flask and make the volume up to the calibration mark with isobutyl methyl ketone. Allow a small precipitate, if present, to settle, draw off about 5 ml of solution with a dry pipette and spray the solution at once into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer. Determine the flame absorbance for the solution. The conditions for this spectrophotometric determination are given in Table I.

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF TIN

Acetylene flow-rate at 15 p.s.i./l min^{-1}	3·8
Nitrous oxide flow-rate at 30 p.s.i./l min^{-1}	5·0
Wavelength for use with tin lamp/nm	224·6
Slit width/mm	0·06
Lamp current/mA	8
Distance of centre of light path above burner/mm	8

Prepare a calibration graph corresponding to 0 to 0·05 per cent. of tin in an alloy by adding 1-g amounts of Specpure iron to each of six beakers followed by 0, 1, 2, 3, 4 and 5 ml of standard tin solution B. Treat these standards in exactly the same way as described for an iron or steel. Determine the flame absorbances of these solutions under the same conditions as those used for the alloys and draw a calibration graph.

NOTES—

1. If the alloy contains more than 0·05 per cent. of tin (500 μg g^{-1}), take a weight of alloy containing less than 500 μg of tin and make the weight up to 1 g with Specpure iron.
2. If preferred, ammonium thiocyanate can be used throughout instead of potassium thiocyanate.
3. The organic phase should not be left for longer than 2 hours before being concentrated by distillation.

TESTS FOR INTERFERING ELEMENTS—

It was appreciated that certain other elements besides tin would be partly extracted into the organic phase when the above method was used. Various weights of twenty-six elements, most of which might be present in steels, were subjected to the extraction procedure. These inorganic species were originally present in 50 ml of an aqueous solution that was 0·5 M in both hydrochloric acid and potassium thiocyanate and 8 per cent. w/v in ascorbic acid. The aqueous solution was shaken with 50 ml of isobutyl methyl ketone and the extent of extraction was found by determining the amount of each element left in the aqueous phase by well established analytical procedures. These were mainly atomic-absorption spectrophotometric methods, but methods involving absorption spectrophotometry with solutions, gravimetry and titrimetry were also used. The extents of extraction of twenty-

TABLE II

EXTENTS OF EXTRACTION OF VARIOUS INORGANIC SPECIES INTO ISOBUTYL METHYL KETONE FROM 0·5 M HYDROCHLORIC ACID - 0·5 M POTASSIUM THIOCYANATE - 8 PER CENT. W/V ASCORBIC ACID SOLUTION

Inorganic species	Extent of extraction, per cent.	Amount originally present in aqueous phase/mg
Aluminium(III)	0	10
Antimony(V)	5	10
Arsenic(V)	0	10
Bismuth(III)	0	5
Boron(III)	1	10
Calcium(II)	0	10
Chromium(III)	0	200
Cobalt(II)	67	100
Iron(III)	6	1000
Lead(II)	0	10
Magnesium(II)	0	10
Manganese(II)	1	100
Molybdenum(VI)	78	10
Nickel(II)	1	100
Niobium(V)*	2	10
Phosphorus(V)	0	10
Selenium(VI)	0	10
Sulphur(VI)	0	10
Tellurium(VI)	0	10
Tin(IV)	99·9	10
Titanium(IV)*	5	10
Vanadium(V)	27	10
Zinc(II)	99	10

* The aqueous phase contained a trace amount of fluoride.

three of these elements are shown in Table II. The other three inorganic species, *viz.*, copper(II), silver(I) and tungsten(VI), formed precipitates.

It was found that 1 and 10-mg amounts of copper(II) both produced a precipitate of copper(I) thiocyanate, which dissolved completely in the organic phase for 1 mg of copper and partly for 10 mg of copper. With 1 mg of copper, the extent of extraction into the isobutyl methyl ketone layer was greater than 99 per cent. A 10-mg amount of silver(I) produced a precipitate of silver chloride, while 1, 10 and 100-mg amounts of tungsten(VI) produced a cloudiness in the aqueous phase, a slight precipitate and a heavy precipitate, respectively. This precipitate from tungsten(VI) was presumably hydrated tungstic acid; when it was removed from the aqueous phase by filtration and the aqueous phase was shaken with isobutyl methyl ketone, the organic phase was colourless, which indicated that no tungsten had been extracted.

It can be seen from Table II and the preceding paragraph that nine elements are extracted into isobutyl methyl ketone to the extent of 5 per cent. or more, *viz.*, tin, iron, antimony, cobalt, copper, molybdenum, titanium, vanadium and zinc.

The possible interfering effects of the last seven of the above elements were tested for by replacing x g of a 1-g sample of Specpure iron by x g of each element, where $100x$ is the maximum percentage of the element that is likely to be present in a ferrous alloy, by adding 300 μg of tin to the sample and by determining the tin content of the simulated alloy by the described method. The amounts of tin found in each instance are shown in Table III.

TABLE III

RECOVERY OF 300 μg OF TIN ADDED TO SAMPLES OF SIMULATED ALLOYS CONTAINING POSSIBLE INTERFERING ELEMENTS

	Amount of element added/mg	Amount of tin found/μg
Antimony	5	305
Cobalt	100	295
Copper*	10	300
Molybdenum	50	300
Titanium	10	295
Vanadium	20	300
Zinc	5	295

* A suspension of copper(I) thiocyanate in the organic phase was removed by filtration through Whatman 1 PS paper before concentration of this phase.

The results indicate that no interfering effects occur. The slight variations from 300 μg are statistical in nature, as the limit of detection for tin is about 10 μg.

A solution containing 300 μg of tin and 10 mg of tungsten was subjected to the solvent-extraction and concentration procedure, and the tin was determined by atomic-absorption spectrophotometry, the precipitate of hydrated tungstic acid having been removed from the aqueous phase by filtration. Amounts of tungsten up to 10 mg had no effect on the quantitative recovery of tin but with greater amounts of tungsten the recovery of tin was low, presumably because tin was co-precipitated on larger precipitates of hydrated tungstic acid.

RESULTS FOR THE ANALYSIS OF IRONS AND STEELS

The calibration graph for the determination of tin in metal samples passed through the origin and curved down slightly towards the concentration axis. There was no tin in the blank. From this calibration graph, the concentration of tin that produced 1 per cent. absorption was established as 0·8 μg ml^{-1}.

The results for the determination of tin in twelve British Chemical Standard iron and steel samples are shown in Table IV.

Precision data were determined for two alloys, namely B.C.S. 206/1 cast iron and B.C.S. 239/3 carbon steel. The standard deviations from the means for ten determinations in each instance were 0·0004 and 0·0006 per cent., respectively.

DISCUSSION

The results for the twelve alloys examined are considered to be good, all average results being in good agreement with the certificate values. The limit of detection is about 0·0010 per cent. The standard deviation of approximately 0·0005 per cent. was satisfactory for the

TABLE IV

TIN CONTENTS OF METAL SAMPLES DETERMINED BY THE DESCRIBED METHOD

Alloy		Tin content by this method, per cent.	Average tin content by this method, per cent.	Certificate value, per cent.
B.C.S. No.	Type			
149/3	High purity iron	0·0015, 0·0010, 0·0015, 0·0015	0·0015	<0·002
206/1	Cast iron	0·0040, 0·0035, 0·0045, 0·0040	0·0040	~0·005
218/3	Carbon steel	0·0410, 0·0405, 0·0415, 0·0410	0·0410	0·042
239/3	Carbon steel	0·0305, 0·0290, 0·0290, 0·0300	0·0295	0·030
320	Mild steel	0·0875, 0·0860, 0·0880, 0·0860	0·0870	0·085
321	Mild steel	0·0135, 0·0135, 0·0130, 0·0135	0·0135	0·014
322	Mild steel	0·235, 0·245, 0·245, 0·230	0·240	0·24
323	Mild steel	0·0245, 0·0240, 0·0250, 0·0255	0·0250	0·024
324	Mild steel	0·130, 0·145, 0·140, 0·130	0·135	0·13
325	Mild steel	0·0465, 0·0455, 0·0460, 0·0450	0·0455	0·046
219/3	Ni - Cr - Mo alloy steel	0·0160, 0·0155, 0·0165, 0·0170	0·0165	~0·016
224/1	Cr - V alloy steel	0·0100, 0·0105, 0·0120, 0·0100	0·0105	~0·01

determination of tin in these irons and steels, but, if necessary, the standard deviation could be improved by using scale expansion and a recorder to determine absorbances. In this study the absorbances were read directly from the absorbance scale on the instrument without scale expansion.

However, it is essential that the analysis be completed as rapidly as possible after the tin has been extracted into isobutyl methyl ketone as the thiocyanate complex. Thiocyanic acid is not particularly stable in the organic phase. When the solution is evaporated to a small volume in the distillation flask, a yellowish brown precipitate is produced. Most of this precipitate is left in the flask when 7 ml of solution are decanted into the 10-ml calibrated flask. Any precipitate that enters the flask is allowed to settle for 2 minutes before 5 ml of the solution are withdrawn to be sprayed immediately into the flame. These 5-ml volumes of solution will slowly become cloudy if they are allowed to stand before spraying. The precipitate does not appear to absorb any tin.

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The Atomic-absorption Spectrophotometric Determination of Total Aluminium in Steel after its Dissolution in a Pressure Bomb

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A method is described for the determination of 0·001 to 0·14 per cent. of total aluminium in irons and steels, which does not involve fusion of an oxide residue. The iron or steel is completely dissolved by first subjecting it to conventional treatment with acid in an open beaker and then to attack by acid in a PTFE-lined bomb at 200 °C. The oxide residue is completely dissolved by attack in the bomb with hydrochloric acid alone or with a mixture of hydrochloric and hydrofluoric acids, the latter solvent being preferred. Iron(III) is extracted from the solution of steel, 6 M in hydrochloric acid, with isobutyl methyl ketone and aluminium is then extracted from the aqueous phase buffered at pH 4·7 with acetylacetone. The concentration of aluminium in the organic phase is determined by atomic-absorption spectrophotometry with a nitrous oxide - acetylene flame. Good results were obtained for the determination of aluminium in eleven standard irons and steels.

ALUMINIUM in steel exists in acid-soluble forms, which include elemental aluminium, and in forms that are insoluble in boiling acid. These acid-insoluble forms are corundum, α-aluminium oxide, and probably aluminium oxide associated with calcium oxide or silicon dioxide, or both. The small amount of acid-insoluble residue is usually brought into solution by fusion with sodium carbonate or with alkali-metal hydrogen sulphate, and the dissolved melt is combined with the initial solution before the determination of total aluminium.

The dissolution procedure would be improved if the fusion step were eliminated. Ito[1] has shown that many minerals that cannot be completely dissolved by attack with acid in an open beaker can be conveniently dissolved by attack with acid in a PTFE-lined bomb at a temperature of 240 °C. We therefore decided to investigate the possibility of dissolving the oxide, which cannot be dissolved by the usual attack with acid, in a similar bomb without the necessity of filtering off the insoluble residue.

We have found that the normally insoluble oxide is dissolved in a pressure bomb and the results of our study are described in this paper. The total aluminium in the solution from the bomb was determined by atomic-absorption spectrophotometry. The instrument at our disposal was a Unicam SP90, Series 1, atomic-absorption spectrophotometer, for which the concentration of aluminium in aqueous solution that produced 1 per cent. absorption was 3 μg ml^{-1}. As the required method had to have a limit of detection of 0·001 per cent., which corresponds to 0·1 μg ml^{-1} for a 1 per cent. m/V solution of the steel, it was necessary to introduce a concentration step for the aluminium. For mild steels, it should be possible to remove iron, the base element, by solvent extraction of iron(III) into isobutyl methyl ketone from 6 M hydrochloric acid and to evaporate the aqueous phase to a small volume in order to obtain a concentration of aluminium that is suitable for atomic-absorption spectrophotometry. However, it was desirable that the method should also be applicable to stainless steels and it was felt that the most satisfactory approach was to remove the iron(III) from a solution of the steel in 6 M hydrochloric acid with isobutyl methyl ketone and then to extract the aluminium as its neutral trisacetylacetonato complex into acetylacetone from an acetate buffer at pH 4·7. It was known that certain elements would at least partially accompany the aluminium into the organic phase, but all of the chromium(III) and most of the nickel(II) would remain in the aqueous phase.[2]

Treatment of the dissolved steel *plus* the small residue containing aluminium in oxide form with approximately 9 M hydrochloric acid in the PTFE-lined bomb at 200 °C for 2½ hours resulted in complete decomposition of the oxide, and the results of applying such a method to the analysis of ten steels are reported and discussed later in the paper. However, this method suffers from the disadvantage that, on longer treatment in the bomb, a small

proportion of the aluminium, which was completely in solution after 2½ hours of heating, is adsorbed on the small silica precipitate and low results for total aluminium are obtained.

To overcome this problem, further work has been undertaken with a mixture of hydrochloric and hydrofluoric acids in the bomb. Dissolution of oxide is complete after heating for 2 hours at 200 °C and the silica is retained in solution as fluorosilicic acid. Heating with the mixture of acids for periods in excess of 2 hours had, as expected, no effect on the amount of aluminium that remained in solution. With the mixture of acids it was, however, necessary to remove the hydrofluoric acid from solution by heating the solution with sulphuric acid to fumes of sulphur trioxide before extracting the aluminium into acetylacetone as its acetylacetonate. The presence of fluoride in the aqueous phase inhibits the extraction of trisacetylacetonatoaluminium(III) into the organic phase.

Two methods are therefore described for the determination of 0·001 to 0·14 per cent. of total aluminium in irons and steels.

Experimental

Apparatus—

A Unicam SP90, Series 1, atomic-absorption spectrophotometer was used with a nitrous oxide - acetylene flame. With scale expansion, a Honeywell 10-mV recorder was used.

The pressure bomb was made of stainless steel and was cylindrical in shape with a screw top. It contained a PTFE liner made from a 150-ml PTFE beaker with a circular PTFE disc serving as a lid. The bomb was almost identical in design with that described by A. Hodkinson and R. H. Jenkins (unpublished work). The capacity of the PTFE liner was 85 ml.

Reagents—

Hydrochloric acid, sp. gr. 1·18.
Hydrofluoric acid, 40 *per cent.* m/m.
Nitric acid, sp. gr. 1·42.
Sulphuric acid, sp. gr. 1·84.
These acids were of analytical-reagent grade.

Sodium hydroxide solution, 3 M *and* 5 M—Dissolve 60 g and 100 g, respectively, of analytical-reagent grade sodium hydroxide pellets in water and dilute the solutions to 500 ml with water.

Acetylacetone—General-purpose reagent. Redistil it before use.

Isobutyl methyl ketone—General-purpose reagent.

Ammonium aluminium sulphate—Analytical-reagent grade.

Iron metal—Specpure quality (Johnson Matthey Chemicals Ltd.).

Other metals and salts used were of analytical-reagent grade or of Specpure quality.

Standard aluminium solution A, approximately 1000 $\mu g\ ml^{-1}$—Dissolve 1·679 g of ammonium aluminium sulphate in water and dilute the solution to 100 ml with water. Determine the true concentration of aluminium in this solution titrimetrically with EDTA.[3] Alternatively, a standard aluminium solution can be made from aluminium metal of Specpure quality.

Standard aluminium solution B, approximately 100 $\mu g\ ml^{-1}$—Dilute 10 ml of solution A to 100 ml with water.

Standard aluminium solution C, approximately 10 $\mu g\ ml^{-1}$—Dilute 10 ml of solution B to 100 ml with water.

Methods

I. Determination of total aluminium after dissolution of the steel with hydrochloric acid—

To 1·000 g of steel in a PTFE liner, add 12 ml of concentrated hydrochloric acid followed by 3 ml of concentrated nitric acid and heat the mixture gently to dissolve the steel (Note 1). Evaporate the solution to the first appearance of solid iron(III) chloride.

Note 1—

If the alloy contains more than 0·05 per cent. of aluminium (500 $\mu g\ g^{-1}$), take an amount of alloy containing less than 500 μg of aluminium and make it up to 1 g with Specpure iron.

Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution to the first appearance of the solid iron(III) chloride. Repeat this operation. Wash any solution on the upper side of the liner into the bottom with 3 ml of concentrated hydrochloric acid and add a further 5 ml of this acid. Place the liner in the bomb, cover the liner with the PTFE lid and close the bomb by screwing on the stainless-steel lid by hand only. Heat the bomb in an oven at 200 °C for 2½ hours. Remove the bomb from the oven and cool it to room temperature under a tap.

Transfer the contents of the liner to a 150-ml beaker with 10 ml of concentrated hydrochloric acid and evaporate the solution to about 10 ml. Dilute the solution to 50 ml with 6 M hydrochloric acid and transfer the diluted solution into a separating funnel. Remove most of the iron from this aqueous phase by shaking it twice with 25-ml volumes of isobutyl methyl ketone. Discard the organic layers. Transfer the aqueous phase to a 100-ml beaker, evaporate the solution to the first appearance of solid and add 5 ml of water. Adjust the pH of the solution to approximately 1 by adding 3 M sodium hydroxide solution dropwise and then to 4·7 by adding sodium acetate crystals. Dilute the solution to approximately 25 ml with water. Extract the aluminium from this aqueous phase in a separating funnel with two 25-ml portions of acetylacetone. Discard the aqueous phase. Combine the organic phases and evaporate this solution to about 7 ml in a small distillation flask on an oil-bath at 150 to 160 °C. Dilute the solution to 10 ml in a calibrated flask with acetylacetone, spray the solution into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer and use the conditions shown in Table I to determine the flame absorbance. With reference to a suitable calibration graph, determine the concentration of total aluminium in the steel.

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF ALUMINIUM

Acetylene flow-rate at 1·05 bar/l min^{-1}	3·2
Nitrous oxide flow-rate at 2·1 bar/l min^{-1}	5·0
Wavelength for use with aluminium lamp/nm ..	309·3
Slit width/mm	0·03
Lamp current/mA	10
Height of centre of light path above burner/mm ..	7

Prepare a calibration graph corresponding to approximately 0 to 0·05 per cent. of aluminium in an alloy by adding a 1-g amount of Specpure iron to each of six beakers followed by 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution B. Treat these standards in exactly the same way as described above for a steel, but omit the treatment in the PTFE-lined bomb. Determine the flame absorbances of these solutions under the same conditions as those used for the alloys and construct a calibration graph.

II. DETERMINATION OF TOTAL ALUMINIUM AFTER DISSOLUTION OF STEEL WITH HYDROCHLORIC AND HYDROFLUORIC ACIDS—

To 1·000 g of steel in a PTFE liner, add 12 ml of concentrated hydrochloric acid followed by 3 ml of concentrated nitric acid and heat the mixture gently to dissolve the steel (Note 1). Evaporate the solution to the first appearance of solid iron(III) chloride.

Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution to the first appearance of the solid iron(III) chloride. Repeat this operation. Wash any solution on the upper side of the liner into the bottom with 3 ml of concentrated hydrochloric acid, then add 4 ml of concentrated hydrofluoric acid. Place the liner in the bomb, cover the liner with the PTFE lid and close the bomb by screwing on the stainless-steel lid by hand only. Heat the bomb in an oven at 200 °C for at least 2 hours. Remove the bomb from the oven and cool it to room temperature under a tap.

Transfer the contents of the liner to a 150-ml beaker with 10 ml of concentrated hydrochloric acid and evaporate the solution to about 10 ml. Dilute the solution to 50 ml with 6 M hydrochloric acid and transfer the diluted solution into a polypropylene separating funnel. Remove most of the iron from this aqueous phase by shaking it twice with 25-ml volumes of isobutyl methyl ketone. Discard the organic layers. Transfer the solution to a 150-ml

PTFE beaker, add 1·5 ml of concentrated sulphuric acid (Note 2), evaporate the solution to fumes of sulphur trioxide and continue the fuming for 5 minutes with occasional agitation of the beaker. Add 10 ml of water to the cooled beaker and adjust the pH of the solution to approximately 1 by adding 5 M sodium hydroxide solution dropwise and then to 4·7 by adding sodium acetate crystals. Dilute the solution to approximately 25 ml with water. Extract the aluminium from this aqueous phase in a separating funnel with two 25-ml portions of acetylacetone. Discard the aqueous phase. Combine the organic phases and evaporate this solution to about 7 ml in a small distillation flask on an oil-bath at 150 to 160 °C. Dilute the solution to 10 ml in a calibrated flask with acetylacetone, spray the solution into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer and use the conditions shown in Table I to determine the flame absorbance. With reference to a suitable calibration graph, determine the concentration of total aluminium in the steel.

Prepare a calibration graph corresponding to approximately 0 to 0·05 per cent. of aluminium in an alloy by adding a 1-g amount of Specpure iron to each of six beakers followed by 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution B. Treat these standards in exactly the same way as described above for a steel, but omit the treatment in the PTFE-lined bomb. Determine the flame absorbances of these solutions under the same conditions as those used for the alloys and construct a calibration graph.

For the determination of aluminium contents of 0·005 per cent. and below, prepare a calibration graph in the same way by using 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution C and ×3 scale expansion with a 10-mV recorder.

NOTE 2—

With stainless steels, use 4 ml of concentrated sulphuric acid.

STUDIES ON HEATING TIMES FOR COMPLETE DISSOLUTION OF OXIDE—

The method for the determination of total aluminium after dissolution of the steel with hydrochloric acid alone (Method I) was applied to steels B.C.S. 321 (0·4-g sample) and B.C.S. 330 (1-g sample) with different periods of heating in the bomb at 200 °C. From Fig. 1, it can be seen that complete dissolution of aluminium is achieved after 2½ hours but that low results for total aluminium in both steels are obtained on longer heating. The results of the following experiments indicated that low results were due to the adsorption of dissolved aluminium on to a precipitate of insoluble silicon dioxide on heating for periods in excess of 2½ hours.

The steel that showed the greater adsorption effects (B.C.S. 330) was dissolved by using Method I and heated in the bomb for 4 hours. The solution was then filtered through a Whatman No. 541 filter-paper and the filtrate analysed to determine aluminium by continuing with Method I. The residue and the filter-paper were digested in a mixture of hydrofluoric and hydrochloric acids; the silicon dioxide passed into solution as fluorosilicic acid and released adsorbed aluminium. The solution was then filtered to remove pulped filter-paper, the second filter-paper was washed and 1·5 ml of concentrated sulphuric acid added to the filtrate. The solution was then analysed to determine aluminium, after evaporation to fumes, pH adjustment, extraction and concentration, by atomic-absorption spectrophotometry as in Method II. When the aluminium contents of the first filtrate and residue were added together, the certificate value for aluminium in B.C.S. 330 steel was obtained. A similar method applied to a filter-paper from the same batch as the one used above showed that it contained a negligible amount of aluminium.

It should be noted that the tailing-off effect in Fig. 1 following Method I with hydrochloric acid alone and heating periods in excess of 2½ hours is much less for B.C.S. 321 than for B.C.S. 330 steel. The ratios of aluminium to silicon present in these steels are 1:0·4 and 1:23, respectively, which is a further indication that adsorption of aluminium on silicon dioxide is responsible for the low results after long periods of heating.

It can be seen from Fig. 1 that when B.C.S. 330 steel was heated for various periods of time in the bomb with hydrochloric and hydrofluoric acids according to Method II, a constant aluminium content was produced when the period of heating was 2 hours or longer. This indicates that if silicon dioxide is brought into solution, no aluminium is lost and the length of time of heating in the bomb need not be strictly adhered to provided that it is a minimum of 2 hours.

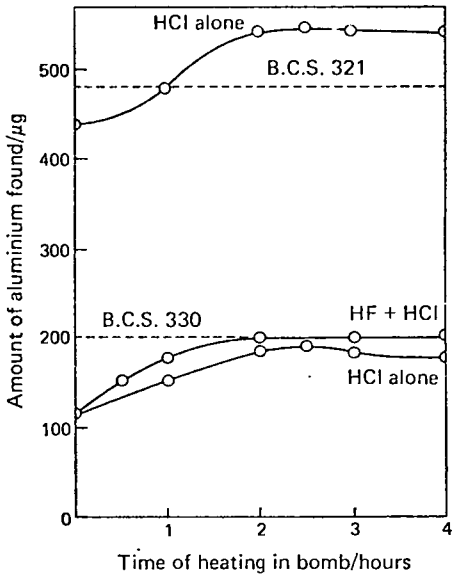

Fig. 1. Effect of time of heating in the bomb on the determination of aluminium in steel. The solid lines correspond to amounts of aluminium found for B.C.S. 321 (0·4-g samples) and B.C.S. 330 (1-g samples) when different acid treatments were used. The upper broken line corresponds to the amount of aluminium expected from the certificate value, which is known only approximately for B.C.S. 321. The lower broken line corresponds to the amount of aluminium expected for B.C.S. 330

TESTS FOR INTERFERING ELEMENTS—

It was appreciated that certain other elements besides aluminium would be partly extracted into the acetylacetone phase when the above methods were used. Various amounts of twenty-four elements, most of which might be present in steels, were subjected to the extraction procedure. These inorganic species were originally present in 25 ml of an aqueous solution that was 0·1 M in both acetic acid and sodium acetate (pH 4·7 buffer). The aqueous solution was shaken with two 25-ml volumes of acetylacetone and the extent of extraction found by determining the amount of each element that remained in the aqueous phase by well established analytical procedures. These were mainly atomic-absorption spectrophotometric methods, but methods that involved absorption spectrophotometry with solutions, gravimetry and titrimetry were also used. The extents of extraction of these elements are shown in Table II.

With the exceptions of iron(III) and aluminium(III), cobalt(II), copper(II), lead(II), manganese(II), molybdenum(VI), nickel(II), niobium(V), tin(IV), titanium(IV), vanadium(V), zinc(II) and zirconium(IV) are each extracted to an extent greater than 5 per cent. However, copper, lead, niobium, tin, titanium, zinc and zirconium are seldom, and in some instances never, present in concentrations greater than 1 per cent. in steel. Cobalt, manganese, molybdenum, nickel and vanadium can be present in greater concentrations, but most of the molybdenum(VI) from a solution of steel would be expected to be extracted into isobutyl methyl ketone from the aqueous 6 M hydrochloric acid solution together with the iron(III).[4] The amount of elements accompanying the aluminium in the final 10 ml of acetylacetone solution is seldom likely to exceed 20 mg, but the possible interfering effects of these elements on the atomic-absorption spectrophotometric determination of aluminium had to be investigated.

TABLE II

EXTENTS OF EXTRACTION OF VARIOUS INORGANIC SPECIES INTO ACETYLACETONE FROM 0·1 M ACETIC ACID - 0·1 M SODIUM ACETATE SOLUTION

Inorganic species	Extent of extraction, per cent.	Amount originally present in aqueous phase/mg
Aluminium(III)	100	10
Antimony(V)	0	10
Arsenic(V)	0	10
Bismuth(III)	0	10
Boron(III)	4	10
Calcium(II)	0	10
Chromium(III)	0	200
Cobalt(II)	11	100
Copper(II)	96	10
Iron(III)	100	1000
Lead(II)	20	10
Magnesium(II)	0	10
Manganese(II)	7	100
Molybdenum(VI)	84	50
Nickel(II)	10	100
Niobium(V)*	48	20
Phosphorus(V)	0	10
Sulphur(VI)	0	10
Thallium(I)	3	10
Tin(IV)	73	10
Titanium(IV)*	46	10
Vanadium(V)	60	10
Zinc(II)	22	10
Zirconium(IV)	90	10

* The aqueous phase contained a trace amount of fluoride.

This investigation was carried out by replacing x g of a 1-g sample of Specpure iron by x g of another element, where $100x$ is the maximum percentage of the element that is likely to be present in a ferrous alloy, then adding 300 μg of aluminium to the sample and determining the aluminium content of the simulated alloy by Method I. This procedure was applied to the twelve elements mentioned above and the amounts of aluminium found in each instance are shown in Table III. The results indicate that no interfering effects occur. The slight variations from 300 μg are statistical in nature.

TABLE III

RECOVERY OF 300 μg OF ALUMINIUM ADDED TO SAMPLES OF SIMULATED ALLOYS CONTAINING POSSIBLE INTERFERING ELEMENTS

Element	Amount added/mg	Amount of aluminium found/μg
Cobalt	100	300
Copper	10	300
Lead	3	300
Manganese	100	298
Molybdenum	50	301
Nickel	100	300
Niobium	20	302
Tin	5	299
Titanium	10	303
Vanadium	20	297
Zinc	2	300
Zirconium	5	301

RESULTS FOR THE ANALYSIS OF IRONS AND STEELS

METHOD I (HYDROCHLORIC ACID ALONE)—

The calibration graph for the determination of aluminium in metal samples was a straight line that intersected the absorbance axis at 0·002 absorbance units, which corresponds to an aluminium blank from the reagents of 0·4 μg ml^{-1}. From this calibration graph, the concentration of aluminium that produced 1 per cent. absorption was calculated as 0·9 μg ml^{-1}.

The results for the determination of aluminium in ten British Chemical Standards samples are given in Table IV.

To obtain precision values, six other samples of B.C.S. 260/3 iron were analysed in addition to the four samples for which results are reported in Table IV. The aluminium contents of these six samples were found to be 0·0019, 0·0023, 0·0020, 0·0018, 0·0014 and 0·0025 per cent. The average of the ten results was 0·0019 per cent. with a standard deviation from the mean of 0·000 36 per cent. The limit of detection of the method is, therefore, 0·0007 per cent.

TABLE IV

ALUMINIUM CONTENTS OF METAL SAMPLES DETERMINED BY METHOD I

The results were obtained on the Unicam SP90 spectrophotometer without scale expansion

Alloy		Aluminium content determined by Method I, per cent.	Average aluminium content by Method I, per cent.	Certificate value, per cent.
B.C.S. No.	Type			
149/3	High-purity iron	0·0039, 0·0031, 0·0030, 0·0036	0·0034	<~0·003
260/3	High-purity iron	0·0020, 0·0017, 0·0014, 0·0016	0·0017	~0·001
320	Mild steel	0·0143, 0·0136, 0·0138, 0·0137	0·0139	0·013
321	Mild steel	0·124, 0·141, 0·139, 0·145	0·137	~0·12
322	Mild steel	0·0921, 0·0942, 0·0939, 0·0953	0·0939	0·093
325	Mild steel	0·0276, 0·0277, 0·0293, 0·0278	0·0281	0·028
328	Mild steel	0·0479, 0·0482, 0·0485, 0·0489	0·0484	0·050
329	Mild steel	0·0574, 0·0590, 0·0584, 0·0581	0·0582	0·058
330	Mild steel	0·0194, 0·0197, 0·0199, 0·0192	0·0196	0·020
224/1	Cr - V steel	0·0054, 0·0045, 0·0043, 0·0060	0·0051	~0·005

METHOD II (HYDROCHLORIC AND HYDROFLUORIC ACIDS)—

The calibration graph for the determination of more than 0·005 per cent. of aluminium in mild and low-alloy steels was a straight line that intersected the absorbance axis at 0·005 absorbance unit, which corresponds to an aluminium blank for the reagents of 1·3 μg ml^{-1}. A similar graph was obtained for stainless steels, but the reagent blank was 3·0 μg ml^{-1}.

The calibration graph for the determination of less than 0·005 per cent. of aluminium in high-purity irons was a straight line. As expected, the aluminium blank for the reagents was 1·3 μg ml^{-1}, as for the mild steels.

The results for the determination of aluminium in eleven British Chemical Standards samples are given in Table V.

To obtain precision values, six other samples of B.C.S. 260/3 iron were analysed in addition to the four samples for which results are reported in Table V. The aluminium contents of these six samples (obtained by using ×3 scale expansion and a recorder) were found to be 0·0019, 0·0016, 0·0016, 0·0017, 0·0017 and 0·0019 per cent. The average of

TABLE V

ALUMINIUM CONTENTS OF METAL SAMPLES DETERMINED BY METHOD II

The results were obtained on the Unicam SP90 spectrophotometer without scale expansion, except those marked with an asterisk

Alloy		Aluminium content determined by Method II, per cent.	Average aluminium content by Method II, per cent.	Certificate value; per cent.
B.C.S. No.	Type			
149/3	High-purity iron	0·0031,* 0·0032,* 0·0034,* 0·0033*	0·0033	<~0·003
260/3	High-purity iron	0·0016,* 0·0018,* 0·0017,* 0·0016*	0·0017	~0·001
320	Mild steel	0·0134, 0·0137, 0·0140, 0·0135	0·0137	0·013
321	Mild steel	0·136, 0·138, 0·134, 0·131	0·135	~0·12
322	Mild steel	0·0937, 0·0931, 0·0941, 0·0934	0·0936	0·093
325	Mild steel	0·0272, 0·0289, 0·0294, 0·0280	0·0284	0·028
328	Mild steel	0·0495, 0·0512, 0·0520, 0·0490	0·0504	0·050
329	Mild steel	0·0581, 0·0578, 0·0580, 0·0584	0·0581	0·058
330	Mild steel	0·0211, 0·0200, 0·0196, 0·0197	0·0201	0·020
224/1	Cr - V steel	0·0052, 0·0051, 0·0052, 0·0050	0·0051	~0·005
235/2	Stainless steel + Ti	0·0478, 0·0486, 0·0480, 0·0481	0·0481	~0·048

* Results obtained by using ×3 scale expansion and a recorder.

the ten results was 0·0017 per cent. with a standard deviation from the mean of 0·000 12 per cent. The limit of detection of the method is, therefore, 0·0002 per cent.

Discussion

The results obtained by both methods are considered to be satisfactory. However, unless the silicon content of the steel is less than 0·1 per cent., Method II, involving dissolution of aluminium-containing oxides with hydrochloric and hydrofluoric acids, is recommended because careful control of the period of heating in the pressure bomb is unnecessary provided that it is not less than 2 hours. If results of the highest precision are not required, the flame absorbances can be read on the meter without scale expansion. However, the use of $\times 3$ scale expansion and a recorder for absorbance measurements leads to a significant increase in precision, the limit of detection (twice the standard deviation of ten determinations near the blank level) being 2 $\mu g\ g^{-1}$ by this procedure compared with 7 $\mu g\ g^{-1}$ by visual inspection of the meter.

For 1-g samples of many mild steels, in which the concentration of aluminium is in excess of 0·005 per cent., the second solvent extraction could be eliminated and the aqueous iron-free solution could be adjusted to a volume of 10 ml before spraying it into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer. With stainless steels, the first extraction does not remove chromium(III) and nickel(II) from a 6 M solution of the steel in hydrochloric acid and the double extraction procedure is recommended. When precise results are required for irons or steels containing less than 0·005 per cent. of aluminium, a double extraction procedure is beneficial as a determination of aluminium is three times more sensitive when an acetylacetone solution rather than an aqueous solution is sprayed. Any type of PTFE-lined bomb that will withstand the high pressures produced by heating at 200 °C will be suitable for the dissolution of the aluminium-containing oxides in steel.

We thank BISRA—The Corporate Laboratories of the British Steel Corporation for a grant towards this work. We are indebted to Messrs. A. Hodkinson and R. H. Jenkins of British Steel Corporation, Strip Mills Division, Research Centre, Port Talbot, for sending us a diagram of their pressure bomb.

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The determination of vanadium in steels by atomic absorption spectrophotometry after ion exchange separation

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A method is described for the determination of 0.0005 to 0.0120 per cent of vanadium in steels. The vanadium is separated from iron and other cations using a column of Zeo Karb 225 ion exchange resin and the effluent concentrated by evaporation before an atomic absorption spectrophotometric finish.

Vanadium in steels can be determined titrimetrically (British Standard 1956) but the method lacks precision when the vanadium content of the steel is less than 0.01 per cent. A direct atomic absorption spectrophotometric determination of vanadium in steel, without a preconcentration step for vanadium, would be attractive if the method were sensitive enough. Using the three lines from a vanadium hollow cathode lamp at 318.3, 318.4 and 318.5 nm, the concentration of vanadium in solution which produces 1 per cent absorption is about 1 μg ml^{-1}, which for 1 g of steel in 100 ml of solution corresponds to 0.01 per cent (Slavin 1968). Capacho-Delgado et al (1966) have, in fact, determined vanadium in steel directly with a double beam atomic absorption spectrophotometer with a limit of detection of about 0.005 per cent. With cheaper single beam instruments and scale expansion, Rank Precision Instruments Ltd. (1971) and Cobb et al (1972) have determined vanadium in steel directly with limits of detection of 0.003 per cent and 0.002 per cent respectively. Knight et al (1969) and Husler (1971) have also used atomic absorption spectroscopy to determine vanadium in tool and alloy steels but they were only interested in vanadium contents within the ranges of 1.0 to 3.5 per cent and 1.0 to 4 per cent respectively.

The metallurgist is becoming increasingly interested in the effects of traces of elements on the properties of steels and requests to determine such elements at concentrations as low as 0.001 per cent or even 0.0001 per cent are made. Some mild and alloy steels have vanadium contents considerably less than 0.01 per cent. In order to determine vanadium with good accuracy and precision at such low concentrations, using an atomic absorption spectrophotometric finish, it is obviously desirable to concentrate the vanadium in a steel solution before nebulizing the solution into the nitrous oxide-acetylene flame of an atomic absorption spectrophotometer. However, before concentrating the steel solution by evaporation, most of the iron must be removed to prevent it from precipitating from solution. The same applies to chromium and nickel in stainless steels. A reasonably quick method for the separation of vanadium from iron, chromium and nickel is, therefore, required before applying atomic absorption spectroscopy to the determination of less than 0.01 per cent of vanadium in steels.

Vanadium (V) in dilute acid solution is held weakly by strongly acidic cation exchange resins while divalent and trivalent cations are held much more strongly. From 1M hydrochloric acid, iron (III) and nickel (II) are retained much more readily by the cation exchange resin AG 50 W – X8 than is vanadium (V) (Strelow 1960). Chromium (III) behaves peculiarly when absorbed on cation exchange resins from dilute hydrochloric acid solutions. Part of the chromium is held strongly by a column of the resin while the rest is readily removed on passing a small volume of dilute hydrochloric acid through the column. Undoubtedly this phenomenon is due to the inert nature of chromium (III) complexes. When chromium (III) is heated in hydrochloric acid solutions, mixtures of aquocomplexes of different charge are produced. Equilibrium between these complexes at room temperature is slow. For this reason nitric or perchloric acid solutions of chromium (III) are preferred in ion exchange studies.

Fritz et al (1962) have found that aluminium (III), bismuth (III), cobalt (II), copper (II), iron (III), manganese (II), nickel (II), lead (II), titanium (IV) and zirconium (IV) can be seperated from vanadium (IV) or (V) by absorbing the cations on a column of Dowex 50 W – X8 from 0.1 M nitric or perchloric acid and eluting the vanadium as its vanadium (V) – hydrogen peroxide complex with 0.01 M perchloric or sulphuric acid containing 1 per cent of hydrogen peroxide. Molybdenum (VI) and tungsten (VI) accompany the vanadium (V). By increasing the acid strength of the eluant to 0.5 to 1 M in the presence of peroxide, titanium (IV) is quantitatively eluted from the column.

This separation of vanadium from many of the other elements in steel is to be expected from a study of the equilibrium distribution coefficients of over forty cations between the cation exchange resin AG 50 W – X8 and solutions of nitric or sulphuric acid (Strelow et al 1965), or perchloric acid (Strelow et al 1972) of concentrations varying from 0.1 to 4.0 N.

A method is now described for the determination of trace amounts of vanadium in steels. It is based on the ion exchange

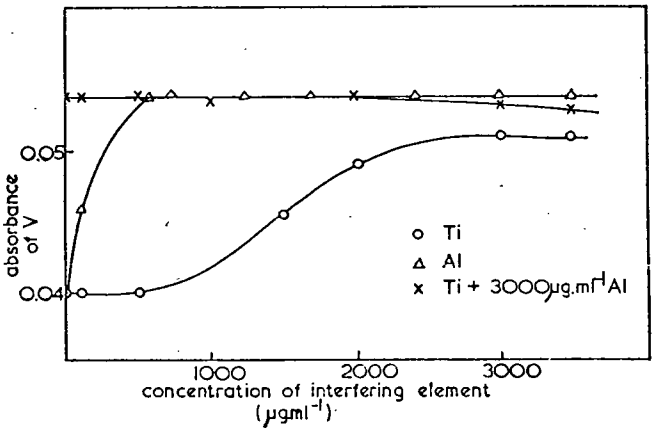

Figure 1. Interferences of aluminium (III) and titanium (IV) on the flame absorbance for 30 μg ml^{-1} of vanadium (V) and the elimination of titanium (IV) interference with 3,000 μg ml^{-1} of aluminium (III).

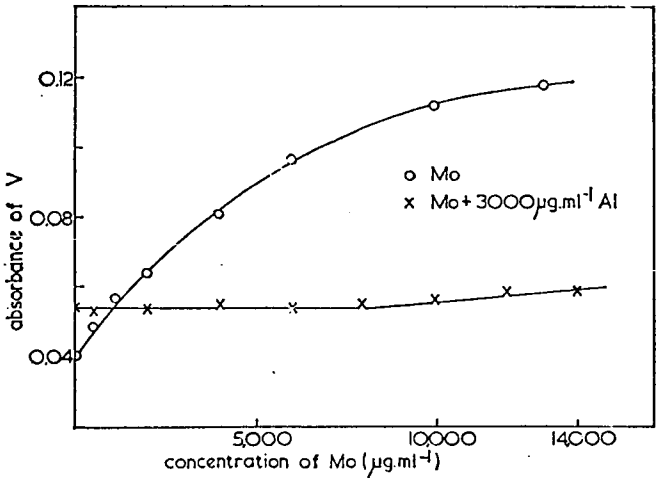

Figure 2. Interference of molybdenum (VI) on the flame absorbance for 30 μg ml^{-1} of vanadium (V) and its elimination with 3,000 μg ml^{-1} of aluminium (III).

separation of vanadium (V) from iron (III) ions and other cations, the concentration of vanadium in the effluent from the ion exchange column, and its determination by atomic absorption spectrophotometry.

Experimental

Atomic absorption spectrophotometer

A Unicam SP90 Series 1 was used with a nitrous oxide – acetylene burner.

Column of cation exchange resin

A column of Zeo Karb 225, 14 – 52 mesh and 40 cm long, was prepared in the hydrogen form in a glass tube of 2 cm diameter. When not in use the resin was kept under 0.75 M hydrochloric acid.

Reagents

Hydrochloric acid, sp. gr. 1.18, analytical reagent grade.

Nitric acid, sp. gr. 1.42, analytical reagent grade.

Vanadium pentoxide, Specpure quality, Johnson Matthey & Co. Ltd.

Standard vanadium solution A (1,000 μg ml^{-1}) – dissolve 0.1785 g of vanadium pentoxide in 5 ml of concentrated hydrochloric acid plus 1 ml of concentrated nitric acid. Boil the solution gently until the volume is about 3 ml. Add 1 ml of 100 volume hydrogen peroxide solution and dilute to 100 ml in a graduated flask.

Standard vanadium solution B (100 μg ml^{-1}) – dilute 10 ml of standard vanadium solution A to 100 ml.

Eluting solution for the column – to 500 ml of 1.8 M hydrochloric acid add 500 ml of water saturated with chlorine.

Aluminium sulphate solution (3,000 μg ml^{-1} of aluminium and 0.5 M in hydrochloric acid) – dissolve 9.3 g of A.R. hydrated aluminium sulphate in 0.5 M hydrochloric acid and dilute to 250 ml with the same acid.

Method for the determination of trace amounts of vanadium in steels

To 1 g of steel, accurately weighed, in a 100 ml beaker add 12 ml of concentrated nitric acid followed cautiously by 3–4 ml of concentrated hydrochloric acid (Note 1). When the vigorous reaction has ceased, heat gently for 5 minutes and evaporate the solution to the first appearance of solid. Add 25 ml of saturated chlorine water to the cooled beaker and dilute to approximately 50 ml with water (Note 2). Allow the solution to stand for 5 minutes.

Add the solution to the column of ion exchange resin and discard the 50 ml of solution which is thus displaced. Pass 250 ml of eluting solution down the column and collect the effluent in a 600 ml beaker. Pass 40 ml of 4.5 M hydrochloric acid down the column and collect the effluent also in the beaker (Note 3).

Evaporate the effluent containing vanadium (V) almost to dryness and take up the residue in 10 ml of concentrated hydrochloric acid. Transfer the solution to a 100 ml beaker. Wash the 600 ml beaker with water and transfer the washings to the 100 ml beaker. Evaporate the solution just to dryness, dissolve the residue in 3 ml of aluminium sulphate solution, add 4 drops of saturated chlorine water and dilute to 5 ml in a graduated flask with aluminium sulphate solution (Note 4).

Nebulize the solution into the nitrous oxide – acetylene flame of the atomic absorption spectrophotometer using the conditions given in Table I. Obtain percentage absorption on the meter using two times scale expansion. Convert to flame absorbance and determine the concentration of vanadium in the solution from steel from a calibration graph of flame absorbance versus concentration for a series of standard solutions sprayed at the same time.

Calibration graph

Add 0, 0.4, 0.8, 1.2, 1.6 and 2.0 ml of standard vanadium solution B to six 10 ml graduated flasks. Add 8 drops of chlorine water to each flask and dilute to the marks with aluminium sulphate solution. Spray the solutions into the nitrous oxide – acetylene flame of the atomic absorption spectrophotometer and construct the calibration graph.

Table I

Instrumental conditions for the determination of vanadium

Acetylene flow rate at 15 psi, 1 min^{-1}	3.6
Nitrous oxide flow rate at 30 psi, 1 min^{-1}	5.0
Wavelength for use with vanadium lamp, nm	318.4
Lamp current, mA	15
Slit width, mm	0.05
Height of centre of light path above burner, mm	9
Scale expansion	X2

Note 1 – The steels would not dissolve in nitric acid alone so the minimum amount of hydrochloric acid, needed to bring about solution, was added. When the dissolution procedure, described in the method, was applied both to 0.2 g of chromium (as chromic chloride) and a stainless steel, all of the chromium was retained by the column of ion exchange resin. Obviously by this procedure no neutral species or singly charged cations of chromium, which would pass rapidly through the column, were produced.

Note 2 – For success in the ion exchange separation the vanadium must be in the +5 oxidation state. The vanadium is usually retained in this state by adding an excess of hydrogen peroxide to the solution. However it was found in this investigation that the decomposition of hydrogen peroxide was catalysed in the presence of iron (III) with the production of bubbles of oxygen in the column of ion exchange resin. Chlorine water was found to be a suitable alternative oxidant.

Note 3 – Regenerate the column by passing about 1 litre of 4.5 M hydrochloric acid through the column followed by 250 ml of 0.75 M hydrochloric acid.

Table II

Results for the determination of trace amounts of vanadium in steels

BCS No.	*Type of steel*	*Concentration of vanadium found by this method (%)*					*Approx. vanadium content on certificate (%)*
		Sample 1	*Sample 2*	*Sample 3*	*Sample 4*	*Average*	
†320	M.S.*	0.0033	0.0037	0.0035	0.0031	0.0034	0.004
321	M.S.	0.0061	0.0063	0.0058	0.0064	0.0062	0.004
322	M.S.	0.0093	0.0090	0.0094	0.0087	0.0091	0.008
323	M.S.	0.0080	0.0083	0.0090	0.0086	0.0085	0.008
†324	M.S.	0.0043	0.0045	0.0039	0.0038	0.0041	0.004
325	M.S.	0.0049	0.0052	0.0054	0.0048	0.0051	0.004
§212/1	0.2% Pb	0.0120	0.0110	0.0113	0.0115	0.0115	<0.01
§239/3	0.3% C	0.0110	0.0098	0.0096	0.0103	0.0102	<0.01
†219/3	Ni-Cr-Mo	0.0030	0.0027	0.0032	0.0033	0.0031	0.004

§ 0.5 g sample + 0.5 g Specpure iron was used.
* M.S. is mild steel.

Note 4 – Molybdenum (VI) and titanium (IV) will accompany anadium (V) in the effluent and both were found to enhance he flame absorbance for vanadium as shown in Figures 1 and 2. However, as is also shown in the figures, the interference effects f not more than 8,000 μg ml^{-1} of molybdenum and 2,000 μg ml^{-1} f titanium are eliminated on the addition of 3,000 μg ml^{-1} of luminium. These concentrations of molybdenum and titanium n the final solutions correspond to 4 per cent of molybdenum nd 1 per cent of titanium in a steel. The addition of aluminium s an interference suppressant for vanadium was reported by obb et al (1972). The addition of 3,000 μg ml^{-1} of aluminium o the vanadium solution also leads to a constant enhancement f the vanadium absorbance of 35 per cent.

The method described above was applied to the determination f vanadium in nine British Chemical Standard Steels, each alloy eing analysed four times.

Results and discussion

he blank solution for the calibration grapn, i.e. the solution ontaining no added vanadium, had zero flame absorbance. The alibration graph for 0 to 20 μg ml^{-1} of vanadium was a slight urve concave to the concentration axis. The concentration of anadium corresponding to 1 per cent absorption was 2.6 μg l^{-1} (13 μg g^{-1} of steel).

The results for the determination of trace amounts of vanadium n the nine steels are shown in Table II.

The standard deviation of errors from the means for all samples is 0.00033 per cent. For alloys marked with a dagger (†), of vanadium content less than 0.005 per cent, the standard deviation of errors from the means is 0.00026 per cent. Hence the limit of detection is 0.0005 per cent.

These results are considered to be satisfactory. With a more expensive atomic absorption spectrophotometer it should be possible to lower the limit of detection to 0.0001 per cent. The total time required for analysing a steel is about 100 minutes but approximately 50 minutes of this time is taken up in evaporating the effluent from the column almost to dryness and the analyst can be employed on other work for most of this time. About 90 minutes are required for regeneration of the column. It seems likely that similar methods could be developed for the determination of trace amounts of molybdenum and titanium in steels.

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The Determination of Iridium and Ruthenium in Rhodium Sponge by Solvent Extraction Followed by Atomic-absorption Spectrophotometry*

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A method is described for the determination of trace amounts of iridium and ruthenium in rhodium sponge. The sponge is dissolved by treatment with concentrated hydrochloric acid and sodium chlorate in a sealed glass tube at 250 °C. Chloro-complexes of rhodium and other noble metals are produced. From such a solution, 2 M in hydrochloric acid, iridium and ruthenium are extracted into chloroform that is 1 per cent. *m/V* in methyltriphenylphosphonium chloride; rhodium is not extracted. The organic phase is evaporated to dryness and the residue dissolved in acetonitrile containing lithium perchlorate, which is the interference suppressant for the subsequent determination of iridium and ruthenium by atomic-absorption spectrophotometry.

Osmium can be determined in rhodium sponge in a similar manner if precautions are taken so as to prevent loss of osmium when the tube is opened. The results are in good agreement with those obtained by emission spectrography and the limits of detection for iridium and ruthenium in the sponge are 7 and 4·5 $\mu g\ g^{-1}$, respectively.

A COMPLEX series of chemical operations is required for the preparation of pure rhodium sponge from ore samples. In the final stages of the refining process rhodium sponge can be produced that contains trace amounts of other noble metals. The efficiency of the process can be ascertained by determining the iridium and ruthenium contents of the sponge. When this work was started in 1972, the detection limits for the spectrographic determination of platinum, ruthenium, osmium and iridium in rhodium sponge were 5, 30, 30 and 40 $\mu g\ g^{-1}$, respectively. It was felt that the detection limits for iridium, osmium and ruthenium could be improved by solvent extraction of these trace elements from an aqueous solution of the rhodium metal into an organic solvent, and subsequent spraying of the organic solvent into the flame of an atomic-absorption spectrophotometer.

Headridge and co-workers have found that the detection limits for the determination of aluminium,[1] antimony,[2] bismuth[3] and tin[4] in steels following solvent-extraction procedures are improved by factors of thirty to sixty compared with methods involving direct atomic-absorption spectrophotometry in aqueous solutions. Slavin[5] states that the concentrations of iridium, osmium and ruthenium that produce 1 per cent. absorption are 8, 1 and 0·3 $\mu g\ ml^{-1}$, respectively, using the atomic lines at 208·9 nm, 290·9 nm and 349·9 nm, respectively. Iridium and ruthenium were determined with the air - acetylene flame but osmium was determined with the nitrous oxide - acetylene flame.

A search of the chemical literature has revealed that 10 to 150 μg of iridium can be separated from 1 to 2 mg of rhodium by means of a single extraction.[6] The extraction was carried out by adding 3 ml of a 2 per cent. solution of tetraphenylphosphonium bromide in water to 15 to 20 ml of iridium(IV) in approximately 0·1 M hydrochloric acid and shaking the mixture for 3 minutes with 10 to 25 ml of chloroform. An extractable ion-association complex is formed with the doubly charged hexachloroiridate(IV) ion, but not with the triply charged hexachlororhodate(III) ion.

Fok[7] has also shown that iridium(IV) can be extracted quantitatively from 0·1 M hydrochloric acid with an equal volume of chloroform containing 1 per cent. *m/V* of tetraphenylarsonium chloride. The hexachlororhodate(III) anion is not extracted. He also states that palladium(II) and (IV), osmium(IV), ruthenium(IV) and platinum(IV) also form extractable compounds with the tetraphenylarsonium cation.

* Presented at a meeting of the Society for Analytical Chemistry and Analytical Division of the Chemical Society, Sheffield, July 12th and 13th, 1973.

If rhodium sponge containing trace amounts of osmium, ruthenium, iridium, palladium and platinum could be brought into solution in hydrochloric acid such that the oxidation states of the chloro-species were rhodium(III), ruthenium(IV), osmium(IV), iridium(IV), palladium(II) or (IV) and platinum(IV), then it seemed likely that trace amounts of iridium, and possibly also ruthenium, osmium, palladium and platinum, could be readily separated from rhodium by solvent extraction.

Dissolution of the noble metals can be achieved by reaction at 250 °C in a sealed tube with chlorine produced from sodium chlorate and concentrated hydrochloric acid.[8] This method of dissolution was used as chloro-complexes of the noble metals are produced. A consideration of the inorganic chemistry of the noble metals indicated that treatment with sodium chlorate and concentrated hydrochloric acid at 250 °C should produce hexachlororhodate(III), hexachloroiridate(IV), hexachloroplatinate(IV), probably mainly hexachlororuthenate(IV) and hexachloropalladate(IV), and probably osmium(VIII) tetroxide together with the dioxotetrachloroosmate(VI) anion, $[OsO_2Cl_4]^{2-}$.[9,10] After diluting the solution to make it 2 M in hydrochloric acid (before the solvent extraction), the osmium will probably be present as a mixture of osmium(VI) and osmium(IV), particularly if the solution is allowed to stand at some stage.

Both osmium tetroxide and the dioxotetrachloroosmate(VI) ion will oxidise the chloride ion in hydrochloric acid to chlorine, the former much more rapidly than the latter. In fact, when standard solutions of rhodium, iridium, ruthenium and osmium in 6 M hydrochloric acid were prepared by the above treatment with concentrated hydrochloric acid and sodium chlorate, and these solutions diluted to make the hydrochloric acid concentration 2 M, it was found that the ultraviolet and visible absorption spectra of the solutions indicated that they contained predominantly the hexachloro-complexes of rhodium(III), iridium(IV), ruthenium(IV) and osmium(IV).

In this paper, a method is described for the dissolution of rhodium metal with concentrated hydrochloric acid and sodium chlorate in a sealed glass tube at 250 °C, and the removal of iridium(IV) and most of the ruthenium(IV) from a solution of the rhodium sponge in 2 M hydrochloric acid by extraction into chloroform containing methyltriphenylphosphonium chloride. The chloroform layer is evaporated to dryness, the residue taken up in acetonitrile, lithium perchlorate added as an interference suppressant and the solution made up to 5 ml with acetonitrile. The concentrations of iridium and ruthenium in this solution, and hence in rhodium sponge, are determined by use of atomic-absorption spectrophotometry. The method should also be suitable for the determination of trace amounts of osmium, if present, in rhodium sponge provided that care is taken to prevent any loss of trace amounts of volatile osmium tetroxide when the tube containing the treated rhodium sponge is opened.

EXPERIMENTAL

APPARATUS—

Pyrex glass tubes, 9 mm in internal diameter, 1·5 mm in wall thickness and sealed at one end, were prepared. These were drawn out near to the open end to form a constriction in the tube with a minimum internal diameter of 2 to 3 mm. The tubes could be sealed by heating these constrictions with an oxy-propane torch. When 100 mg of noble-metal sponge were to be dissolved, the sealed tube was 25 cm long, but for samples of 500 mg, longer tubes (50 cm) were used. Before heating was started, the tube was enclosed in a steel casing with a steel screw-top. The steel casing contained 20 g of calcium carbonate powder in order to neutralise acid, which would escape from the sealed tube in the unlikely event of the tube exploding. A small escape hole for gases was also drilled through the side of the casing.

Atomic-absorption spectrophotometric measurements were made with Unicam SP90 Series 1 and Unicam SP1900 instruments fitted with air - acetylene or nitrous oxide - acetylene burners.

REAGENTS—

Hydrochloric acid, sp. gr. 1·18—Analytical-reagent grade.
Sodium chlorate—General-purpose reagent.
Lithium perchlorate—General-purpose reagent, dried at 100 °C.
Chloroform—Analytical-reagent grade.

Acetonitrile—General-purpose reagent, redistilled at 82 °C before use.

Methyltriphenylphosphonium chloride—This reagent was prepared from methyltriphenylphosphonium bromide (Koch-Light Laboratories Ltd.) by passing an aqueous solution of the salt through a column of De-Acidite FF resin in the chloride form. The effluent was evaporated at 100 °C nearly to dryness and the solid was then dried in an oven at 90 °C for 6 hours.

Rhodium, iridium, ruthenium and osmium sponges—These were of Specpure quality and were supplied by Johnson Matthey Chemicals Ltd.

Potassium hexachloropalladate (IV) and potassium hexachloroplatinate(IV)—These salts were prepared from palladium(II) chloride and platinum(IV) chloride, respectively.

Standard iridium solution A (1000 $\mu g\ ml^{-1}$)—Weigh accurately 100 mg of iridium sponge into a small glass tube, transfer it quantitatively into a Pyrex tube (25 cm long when sealed) and add 5 ml of concentrated hydrochloric acid (sp. gr. 1·18). Immerse the tube in liquid nitrogen or cardice until the contents just start to solidify and then add 0·2 g of sodium chlorate crystals. Remove the tube from the coolant, seal it and allow it to attain room temperature. Place it in a steel casing fitted with a screw-cap and heat in an oven at 250 °C for 6 hours so as to dissolve all of the sponge. Allow the tube to cool to room temperature and cool it again in liquid nitrogen or cardice until the contents just start to solidify. Open the tube by scratching the glass near to the sealed end and giving it a sharp tap. (As the tube breaks, chlorine, under pressure in the tube, may escape.) Transfer the contents into a 100-ml calibrated flask containing 45 ml of concentrated hydrochloric acid, rinse the tube several times with distilled water and make the volume up to the mark so that the concentration of hydrochloric acid in the final solution is approximately 6 M.

Standard iridium solution B (100 $\mu g\ ml^{-1}$)—Dilute 10 ml of solution A to 100 ml with 2 M hydrochloric acid immediately before use.

Standard ruthenium solutions A (1000 $\mu g\ ml^{-1}$) *and B* (100 $\mu g\ ml^{-1}$)—These solutions are prepared in a similar way to the iridium solutions.

Standard rhodium solution (5000 $\mu g\ ml^{-1}$)—This is prepared in a similar way to the above solutions, except that 500 mg of rhodium sponge, 10 ml of concentrated hydrochloric acid and 0·6 g of sodium chlorate are used in a 50 cm long sealed tube.

Standard osmium solution (1000 $\mu g\ ml^{-1}$)—This is prepared in a similar way to the above solutions, but before opening the tube, the contents are solidified completely by immersing the tube in liquid nitrogen. The opened tube is then placed upright in a 100-ml beaker and held clear of the sides of the beaker by means of tongs fitted with glass end-pieces. From a beaker immersed in cardice, 45 ml of cooled, concentrated hydrochloric acid are then added to the tube so as to fill it completely, the excess of acid being added to the 100-ml beaker. A long test-tube is inverted over the glass tube containing the osmium such that the open end of the tube is immersed in the acid in the beaker. This outer tube is used in order to direct into the beaker any solution that may spray from the inner tube as the solid chlorine melts and then vaporises.

The beaker and tubes are allowed to stand until they attain room temperature; as the liquid in the tube expands, it overflows into the beaker. Rinse the outer test-tube with distilled water and collect the rinsings in the beaker. Then transfer approximately 5 ml of liquid from the tube into the beaker with a narrow diameter pipette and rinse the outside of the tube with distilled water, collecting the rinsings in the beaker. Add the contents of the tube to the beaker and rinse the tube with distilled water. Finally, transfer the contents of the beaker into a 100-ml calibrated flask and dilute to the mark. By use of this method no loss of volatile osmium tetroxide can occur.

EXTENTS OF EXTRACTION OF THE NOBLE METALS—

Rhodium—Two extractions with 10-ml volumes of chloroform that was 1 per cent. *m/V* in methyltriphenylphosphonium chloride were carried out on 40 ml of 2 M hydrochloric acid containing 1000 μg of rhodium, prepared from standard rhodium solution. The aqueous solution was diluted to 50 ml. The amount of rhodium in the aqueous phase was determined by atomic-absorption spectrophotometry.

Palladium and platinum—A similar procedure to that for rhodium was applied to solutions of palladium(IV) and platinum(IV) in 2 M hydrochloric acid.

Iridium—Two extractions were carried out with 60-ml volumes of chloroform that was 1 per cent. *m/V* in methyltriphenylphosphonium chloride on 240 ml of 2 M hydrochloric acid containing 3000 μg of iridium, prepared from standard iridium solution A. The aqueous phase was evaporated to dryness and the residue taken up in 5 ml of 2 M hydrochloric acid. The concentration of iridium was determined in this solution by atomic-absorption spectrophotometry.

Ruthenium—A similar procedure was applied to a solution of ruthenium in 2 M hydrochloric acid, prepared from standard ruthenium solution A.

Osmium—A similar extraction procedure was applied to a solution of osmium in 2 M hydrochloric acid prepared from standard osmium solution. As solutions in 2 M hydrochloric acid prepared from the standard osmium solution absorb strongly at 372 nm, solution absorption spectrophotometry was used in order to determine the concentration of osmium remaining in the aqueous phase.

The extents of extraction of the above six elements into chloroform are shown in Table I.

TABLE I

EXTENTS OF EXTRACTION OF NOBLE METALS INTO CHLOROFORM

Element	Amount extracted, per cent.
Rhodium	0
Iridium	100
Ruthenium	90
Osmium	100
Palladium	43
Platinum	93

TENTATIVE METHOD FOR THE DETERMINATION OF IRIDIUM AND RUTHENIUM IN RHODIUM SPONGE—

A tentative method for these determinations could now be devised and was as follows. To 0·5 g of rhodium sponge contained in a Pyrex tube, add 10 ml of concentrated hydrochloric acid. Cool the tube and its contents in liquid nitrogen and add 0·6 g of sodium chlorate, then seal the tube and heat it for a minimum of 6 hours at 250 °C. Open the tube and transfer the contents quantitatively into a 250-ml separating funnel, then add 10 ml of concentrated hydrochloric acid and dilute the solution to 120 ml. Add 30 ml of chloroform that is 1 per cent. *m/V* in methyltriphenylphosphonium chloride to the mixture in the funnel and shake it vigorously for 2 minutes. Allow the layers to separate and transfer the organic phase into a 100-ml beaker, then add 30 ml of chloroform solution and extract again. Combine the chloroform phases and evaporate them to dryness on a steam-bath, as chloroform has unsatisfactory burning characteristics in flames. Take up the residue in 2 ml of acetonitrile and transfer the solution into a 5-ml calibrated flask, washing the beaker with acetonitrile and finally diluting the solution to the mark with the same solvent.

Determine the flame absorbances for iridium and ruthenium in this solution by nebulising the solution into the appropriate flame of an atomic-absorption spectrophotometer. By use of suitable calibration graphs, calculate the concentration of these elements in the rhodium sponge.

ATOMIC-ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM, RUTHENIUM AND OSMIUM—

Iridium—By using the Unicam SP90 spectrophotometer, the 263·9 nm atomic line from an iridium hollow-cathode lamp and an air - acetylene flame, a calibration graph of absorbance *versus* concentration was constructed for iridium (0 to 2000 μg ml^{-1}) in 2 M hydrochloric acid by appropriate treatment of standard iridium solution A. The instrument conditions for this graph are given in Table II.

In order to obtain the calibration graph for iridium in acetonitrile, the following method was used. To six separating funnels add 0, 1, 2, 3, 4 and 5 ml of standard iridium solution B and make up the volumes of the solutions to approximately 40 ml by adding 2 M hydrochloric acid. In each instance extract the solution twice by vigorous shaking with 10-ml volumes of chloroform that is 1 per cent. *m/V* in methyltriphenylphosphonium chloride. Transfer the combined chloroform phases into 100-ml beakers and evaporate to dryness on the steam-bath. Take up the residue in each beaker with 2 ml of acetonitrile and transfer the solutions

into 5-ml calibrated flasks marked 0, 20, 40, 60, 80 and 100 μg ml^{-1} of iridium. Dilute to the marks with the acetonitrile solvent and obtain the absorbance for each solution nebulised into the flame under the conditions given in Table II.

Calibration graphs for iridium in solution in 2 M hydrochloric acid (0 to 250 μg ml^{-1}) and in acetonitrile (0 to 80 μg ml^{-1}) were also obtained by using the Unicam SP1900 spectrophotometer under the conditions given in Table III.

Ruthenium and osmium—By using the Unicam SP90, calibration graphs were also obtained for ruthenium in solution in 2 M hydrochloric acid (0 to 400 μg ml^{-1}) and in acetonitrile (0 to 100 μg ml^{-1}), and for osmium in 2 M hydrochloric acid (0 to 2000 μg ml^{-1}) and in acetonitrile (0 to 200 μg ml^{-1}). The solvent-extraction procedures were identical with those used for iridium. The conditions for the atomic-absorption spectrophotometric determinations are shown in Table II.

TABLE II

INSTRUMENT CONDITIONS FOR THE ATOMIC-ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM, RUTHENIUM AND OSMIUM WHEN USING THE UNICAM SP90 INSTRUMENT

Instrument parameter		Iridium	Ruthenium	Osmium
Flow-rate/l min^{-1}	Air at 30 p.s.i.	5	5	—
	C_2H_2 at 7 p.s.i. (aqueous solution)	1·2	1·4	—
	C_2H_2 at 7 p.s.i. (CH_3CN)	1·0	1·2	—
	N_2O at 30 p.s.i.	—	5	5
	C_2H_2 at 15 p.s.i. (aqueous solution)	—	2·8	3
	C_2H_2 at 15 p.s.i. (CH_3CN)	—	2·6	2·8
Wavelength of line used/nm		263·9	349·8	290·9
Slit width/mm		0·03	0·03	0·03
Lamp current/mA		15	15	15
Distance of centre of light path above burner/mm	Air - C_2H_2	9	5	—
	N_2O - C_2H_2		5	10

Calibration graphs for ruthenium (0 to 100 μg ml^{-1}) and osmium (0 to 400 μg ml^{-1}) in 2 M hydrochloric acid, and for ruthenium (0 to 40 μg ml^{-1}) and osmium (0 to 80 μg ml^{-1}) in acetonitrile, were also obtained by use of the Unicam SP1900 instrument under the conditions given in Table III.

TABLE III

INSTRUMENT CONDITIONS FOR THE ATOMIC-ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM, RUTHENIUM AND OSMIUM WHEN USING THE UNICAM SP1900 INSTRUMENT

Instrument parameter		Iridium	Ruthenium	Osmium
Flow-rate/l min^{-1}	Air at 30 p.s.i.	5	5	—
	C_2H_2 at 10 p.s.i. (aqueous solution)	1·2	1·2	—
	C_2H_2 at 10 p.s.i. (CH_3CN)	0·7	—	—
	N_2O at 30 p.s.i.	—	5	5
	C_2H_2 at 10 p.s.i. (aqueous solution)	—	—	3
	C_2H_2 at 10 p.s.i. (CH_3CN)	—	2·8	2·8
Wavelength of line used/nm		263·9	349·8	290·9
Slit width/mm		0·03	0·03	0·05
Sensitivity		490	580	518
Integration time/s		4	4	4
Lamp current/mA		15	15	15
Distance of centre of light path above burner/mm	Aqueous solution	9	8	10
	CH_3CN	9	10	10

The flow-rates shown in Tables II and III were those found to produce the maximum absorbances for solutions of the noble metals. The nitrous oxide - acetylene flames were lit and extinguished via air - acetylene.

The concentrations of iridium, ruthenium and osmium in 2 M hydrochloric acid and in acetonitrile that produce 1 per cent. absorption using both the Unicam SP90 and Unicam SP1900 atomic-absorption spectrophotometers are shown in Table IV.

TABLE IV

CONCENTRATIONS OF IRIDIUM, RUTHENIUM AND OSMIUM PRODUCING 1 PER CENT. ABSORPTION

Element	Flame type	Sensitivity in aqueous solution/μg ml^{-1}		Sensitivity in acetonitrile/μg ml^{-1}	
		SP90	SP1900	SP90	SP1900
Iridium	Air - C_2H_2	17	16	2·2	1·6
Ruthenium	Air - C_2H_2	14	0·6	20	—
	N_2O - C_2H_2	29	2·5	10·7	0·8
Osmium	N_2O - C_2H_2	65	5	12·5	1·5

For 0·5-g samples of rhodium sponge, the figures in the last column of Table IV correspond to 16, 8 and 15 μg g^{-1} of iridium, ruthenium and osmium, respectively. The limits of detection would be lower than these values and a method based on the tentative method for the determination of iridium, ruthenium and osmium in rhodium sponge will be more sensitive than the spectrographic method (see above). However, before such a method could be applied to rhodium sponges, it was necessary to investigate the possible interfering effects of other extractable noble metals on the absorbances of solutions of iridium, ruthenium and osmium.

INTERFERING EFFECTS OF RUTHENIUM, OSMIUM, PLATINUM AND PALLADIUM ON IRIDIUM—

Twenty solutions, each containing 200 μg of iridium in addition to 200 to 1000 μg of ruthenium, osmium, palladium or platinum, were extracted in a similar way to that described for the iridium in acetonitrile calibration graph. The flame absorbances (air - acetylene flame) of the solutions of iridium containing different amounts of other co-extracted noble metals in acetonitrile were measured on the Unicam SP90 instrument and compared with the flame absorbance of acetonitrile containing iridium alone. All of these added elements affected the iridium absorbance, as shown in Fig. 1.

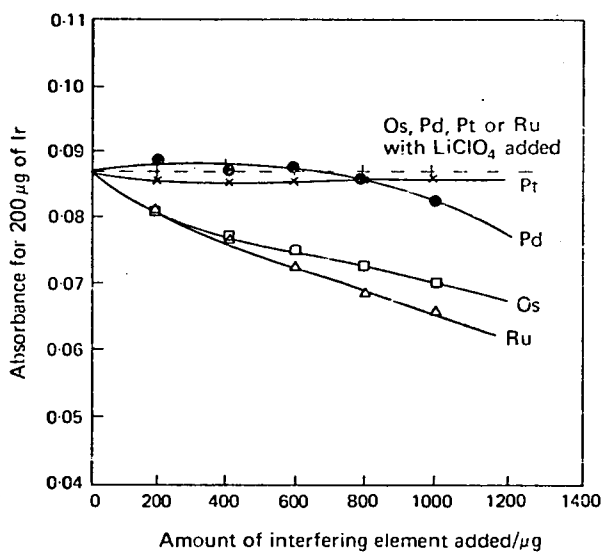

Fig. 1. Effects of extracted osmium, palladium, platinum and ruthenium on the absorbance for extracted iridium. The amounts of elements are those originally present in the aqueous solutions before extraction

INTERFERING EFFECTS OF IRIDIUM, OSMIUM, PALLADIUM AND PLATINUM ON RUTHENIUM—

Twenty solutions, each containing 300 μg of ruthenium in addition to 250 to 1250 μg of iridium, osmium, palladium or platinum, were extracted in a similar way to that described

for the iridium in acetonitrile calibration graph. The flame absorbances (nitrous oxide - acetylene flame) of the solutions of ruthenium in acetonitrile containing different amounts of other co-extracted noble metals were measured on the Unicam SP90 instrument and compared with the flame absorbance of acetonitrile containing ruthenium alone. All of these added elements affected the ruthenium absorbance, as shown in Fig. 2.

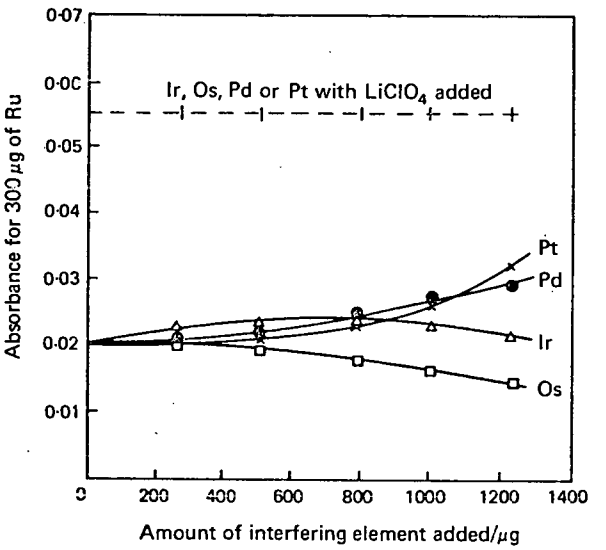

Fig. 2. Effects of extracted iridium, osmium, palladium and platinum on the absorbance for extracted ruthenium. The amounts of elements are those originally present in the aqueous solutions before extraction

INTERFERING EFFECTS OF RUTHENIUM, IRIDIUM, PALLADIUM AND PLATINUM ON OSMIUM—

Twenty solutions, each containing 250 μg of osmium in addition to 250 to 1250 μg of ruthenium, iridium, palladium or platinum, were extracted in a similar way to that described for the iridium in acetonitrile calibration graph. The flame absorbances (nitrous oxide - acetylene flame) of the solutions of osmium in acetonitrile containing different amounts of other co-extracted noble metals were measured on the Unicam SP90 instrument and compared with the flame absorbance of acetonitrile containing osmium alone. Iridium did not interfere but the other added elements affected the osmium absorbance, as shown in Fig. 3.

ELIMINATION OF INTERFERENCES IN THE DETERMINATION OF IRIDIUM, RUTHENIUM AND OSMIUM—

Pannetier and Toffoli[11] successfully used lithium sulphate as an interference suppressant when trace amounts of platinum, iridium, rhodium and palladium were determined in matrices of hexachlororhodic, hexachloroiridic and hexachloroplatinic acids. Lithium perchlorate is readily soluble in non-aqueous solvents and when it was added to solutions of the noble metals in acetonitrile the interferences were eliminated. Thus, 1 ml of a 5 per cent. m/V solution of lithium perchlorate in acetonitrile was added to the solutions of the noble metals in acetonitrile before the volumes were adjusted to 5 ml. The concentration of lithium ions in the solutions to be nebulised was, therefore, approximately 600 μg ml^{-1}. As shown in Figs. 1, 2 and 3, the addition of lithium perchlorate not only removed the interferences due to the other noble metals, but also enhanced the flame absorbances for ruthenium and osmium and allowed these two elements to be determined with considerably greater sensitivity. No enhancement in flame absorbance occurred for iridium when lithium perchlorate was present in the solutions.

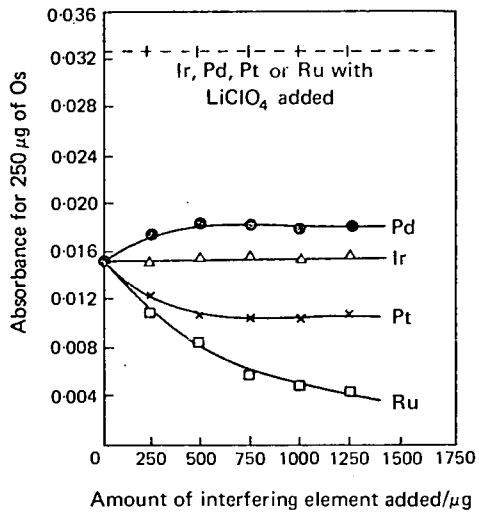

Fig. 3. Effects of extracted iridium, palladium, platinum and ruthenium on the absorbance for extracted osmium. The amounts of elements are those originally present in the aqueous solutions before extraction

FINAL METHOD FOR THE DETERMINATION OF IRIDIUM AND RUTHENIUM IN RHODIUM SPONGE

To 0·5 g of rhodium sponge, containing up to 0·1 per cent. each of iridium and ruthenium, in a Pyrex tube (50 cm long when sealed), add 10 ml of concentrated hydrochloric acid. Immerse the tube in liquid nitrogen or cardice until the contents just start to solidify and then add 0·6 g of sodium chlorate crystals. Remove the tube from the liquid nitrogen, seal it and allow it to attain room temperature. Place it in a steel casing fitted with a screw-cap and heat it in an oven at 250 °C for at least 6 hours so as to dissolve all of the sponge. Allow the tube to cool to room temperature and cool it again in liquid nitrogen or cardice until the contents just start to solidify. Open the tube by scratching the glass near to the sealed end and giving it a sharp tap. (As the tube breaks, chlorine, under pressure in the tube, may escape.)

Transfer the contents of the tube quantitatively into a 250-ml separating funnel, then add 10 ml of concentrated hydrochloric acid and dilute the solution to 120 ml. Add 30 ml of chloroform that is 1 per cent. m/V in methyltriphenylphosphonium chloride to the mixture in the funnel and shake it vigorously for 2 minutes. Allow the layers to separate and transfer the organic phase into a 100-ml beaker, then add 30 ml of chloroform solution and extract again. Combine the chloroform phases and evaporate them to dryness on a steam-bath. Take up the residue in 2 ml of acetonitrile and transfer the solution into a 5-ml calibrated flask. Rinse the beaker with 1 ml of acetonitrile and add the rinsings to the flask, then add 1 ml of a 5 per cent. m/V solution of lithium perchlorate in acetonitrile, ignoring a small precipitate of methyltriphenylphosphonium perchlorate that forms, and dilute the solution to the mark with the same solvent.

Determine the flame absorbances for iridium and ruthenium in this solution by using air - acetylene and nitrous oxide - acetylene flames, respectively, and the instrument conditions outlined in Table III. If the rhodium sponge contains not less than 70 $\mu g\ g^{-1}$ of iridium and 200 $\mu g\ g^{-1}$ of ruthenium, the instrument conditions outlined in Table II can be used. Read off the concentrations of iridium and ruthenium from calibration graphs prepared from solutions, the flame absorbances of which were determined at the same time as those of the solutions prepared from the rhodium sponge samples.

PREPARATION OF THE CALIBRATION GRAPHS—

Iridium—The method is identical with that described under *Iridium* in the section entitled Atomic-absorption spectrophotometric determination of iridium, ruthenium and

osmium, except that a 1-ml volume of a 5 per cent. *m/V* solution of lithium perchlorate in acetonitrile is added to each 5-ml calibrated flask before diluting to the mark.

Ruthenium—The method is identical with that used for iridium except that standard ruthenium solution B is used.

ANALYSIS OF SYNTHETIC MIXTURES OF RHODIUM SPONGE WITH TRACE AMOUNTS OF IRIDIUM, RUTHENIUM AND OSMIUM ADDED—

Seven synthetic mixtures were prepared by adding fixed volumes of standard solutions of iridium and ruthenium to 0·5-g amounts of Specpure rhodium sponge in seven Pyrex tubes. Dissolution was achieved in a similar way to that described in the final method and the iridium and ruthenium contents of these solutions were determined as outlined in the final method. Four of these solutions also contained known trace amounts of osmium, which were later determined by atomic-absorption spectrophotometry in a manner similar to that for iridium, but this osmium was added after the dissolution procedure and before the solvent extraction (see Discussion).

ANALYSIS OF RHODIUM SPONGE SAMPLES—

Eleven samples of rhodium sponge were analysed for iridium and ruthenium contents by means of the final method, as was a 1-g sample of rhodium trichloride.

RESULTS

The sensitivities of the atomic-absorption spectrophotometric determinations of iridium, ruthenium and osmium in acetonitrile containing lithium perchlorate are given in Table V.

TABLE V

CONCENTRATIONS OF IRIDIUM, RUTHENIUM AND OSMIUM PRODUCING 1 PER CENT. ABSORPTION IN ACETONITRILE CONTAINING LITHIUM PERCHLORATE

Element	Flame type	Sensitivity in acetonitrile containing $LiClO_4$/μg ml^{-1} SP90	SP1900
Iridium	Air - C_2H_2	2·2	1·6
Ruthenium	Air - C_2H_2	15	—
	N_2O - C_2H_2	3	0·4
Osmium	N_2O - C_2H_2	7	1

Results for the analysis of synthetic mixtures of rhodium containing trace amounts of iridium, ruthenium and osmium are shown in Table VI. These results are corrected for the trace amount of iridium present in the Specpure rhodium sponge; no ruthenium or osmium could be detected in this sponge. The results for mixtures 1, 2, 3 and 4 were obtained with the Unicam SP90 instrument. The Unicam SP1900 instrument was used in the analysis of mixtures 5, 6 and 7.

TABLE VI

RESULTS FOR THE ANALYSIS OF SYNTHETIC MIXTURES OF RHODIUM CONTAINING TRACE AMOUNTS OF IRIDIUM, RUTHENIUM AND OSMIUM

	Iridium, per cent.		Ruthenium, per cent.		Osmium, per cent.	
Mixture	Added	Found	Added	Found	Added	Found
1	0·060	0·058	0·040	0·041	0·120	0·115
2	0·040	0·037	0·100	0·100	0·080	0·075
3	0·020	0·017	0·020	0·019	0·160	0·150
4	0·100	0·099	0·060	0·061	0·040	0·042
5	0·020	0·022	0·080	0·075	—	—
6	0·080	0·082	0·060	0·065	—	—
7	0·160	0·155	0·020	0·020	—	—

Results for the determination of iridium and ruthenium in rhodium sponges by the described method are given in Table VII, together with results for the spectrographic determination of these elements in the sponges. The atomic-absorption results are the averages of two determinations on each sample.

TABLE VII

COMPARISON OF RESULTS FOR THE DETERMINATION OF IRIDIUM AND RUTHENIUM IN RHODIUM SPONGE BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY AND EMISSION SPECTROGRAPHY

	Iridium content, per cent.		Ruthenium content, per cent.	
Sample	Spectrographic analysis	Atomic-absorption spectrophotometry	Spectrographic analysis	Atomic-absorption spectrophotometry
A	0·1	0·098	0·07	0·0770
B	0·001	N.D.	N.D.	N.D.
C	0·01	0·012	0·020	0·0190
D	0·015	0·014	0·005	0·0060
E	0·007	0·008	0·005	0·0070
F	0·03	0·027	0·007	0·0075
G	0·005	0·010	0·007	0·0080
H	0·03	0·029	0·015	0·0150
J	0·03	0·027	0·001	N.D.
K	0·007	0·008	0·005	0·0055
Specpure sponge	—	0·005	—	N.D.
$RhCl_3.xH_2O$	—	0·042	—	0·0218

N.D. = Not detected.

DISCUSSION

The results obtained for the determination of trace amounts of iridium in actual and simulated rhodium sponge samples are considered to be satisfactory. Only with iridium for sample G is there some discrepancy between the spectrographic and atomic-absorption spectrophotometric results. The limits of detection for the determination of iridium and ruthenium in rhodium sponge were 7 and 4·5 $\mu g\ g^{-1}$, respectively, where the limit of detection is defined as that concentration of the element which gives a signal equal to twice the standard deviation of a series of ten determinations near to the blank level. The spectrographic results were obtained in the laboratories of Johnson Matthey Chemicals Ltd. by using solid samples in a d.c. arc, intensities being recorded photographically on an Ebert 3-m instrument.

Rhodium sponge seldom contains osmium in detectable amounts but if such a determination has to be made, it is advisable to freeze completely the contents of the Pyrex tube by immersing it in liquid nitrogen before it is broken and to treat the contents in the manner specified in the method for preparing a standard solution of osmium. If a known trace amount of osmium is added to 0·5 g of rhodium sponge and the sponge dissolved according to the procedure of the final method, in which the contents of the tube are cooled until they just start to solidify, there is only a 97 per cent. recovery of osmium, presumably because a small amount of volatile osmium tetroxide escapes with the excess of chlorine from the tube when it is broken.

Rhodium sponge is particularly difficult to dissolve, but the use of sealed glass tubes in the dissolution procedure was very helpful. If simple precautions are taken, these tubes are not dangerous and are easy to handle. No explosions occurred when tubes containing 1 g of sodium chlorate and 10 ml of concentrated hydrochloric acid were heated to a maximum temperature of 260 °C. The use of a PTFE-lined steel pressure vessel for the dissolution of rhodium, iridium and ruthenium with sodium chlorate and concentrated hydrochloric acid has been investigated. Unfortunately, neither rhodium nor iridium could be dissolved completely at a temperature of 220 °C on heating for 14 hours. When the temperature was increased, the PTFE started to soften and gases escaped from the pressure vessel. Ruthenium was found to dissolve at 220 °C on treatment in the pressure vessel for 24 hours but iridium still resisted complete dissolution under similar conditions.

It is well known that noble-metal hollow cathodes have complicated emission spectra, and the lack of sensitivity for ruthenium and osmium in atomic-absorption spectrophotometric determinations when the Unicam SP90 instrument was used is due to the inexpensive monochromator of the instrument, which could not resolve the resonance lines from the emission spectra. When iridium was determined, the less sensitive resonance line at 263·9 nm was used as it was less noisy than the primary resonance line at 208·9 nm.

Precipitates slowly formed during the extraction procedure when more than 600 μg of

iridium, 800 μg of ruthenium and 1200 μg of osmium were extracted into 10 ml of chloroform that was 1 per cent. *m/V* in methyltriphenylphosphonium chloride. Therefore, an immediate transfer of the chloroform layer was necessary when the amounts of noble metals exceeded these limits. The precipitates are very soluble in acetonitrile.

The mutual interferences have been eliminated by the addition of lithium perchlorate. Not only were the interferences overcome, but also, for ruthenium and osmium, an enhancement in the absorption signals occurred. The causes of mutual interferences among the noble metals are not understood and very little is known about the mode of action of the reagents that suppress them.

As can be seen from Tables IV and V, the concentrations of iridium, ruthenium and osmium in acetonitrile containing lithium perchlorate that produce 1 per cent. absorption with the Unicam SP1900 instrument are 1·6, 0·4 and 1 μg ml^{-1}, respectively, compared with the best values of 16, 0·6 and 5 μg ml^{-1} for aqueous solutions. If, for a direct method without solvent extraction, a typical concentration of rhodium in aqueous solution is taken as being 1 per cent. *m/V*, then the concentrations of iridium, ruthenium and osmium in rhodium sponge corresponding to 1 per cent. absorption are 1600, 60 and 500 μg g^{-1}, respectively. With the solvent-extraction procedure, the concentrations of iridium, ruthenium and osmium in rhodium sponge corresponding to 1 per cent. absorption are 16, 4 and 10 μg g^{-1}, which is a marked improvement. No scale expansion was used on the Unicam SP1900 instrument in these determinations, but if scale expansion is used it is anticipated that the limits of detection for iridium and ruthenium in rhodium sponge by the described method will be 4 and 1 μg g^{-1}, respectively, or even better.[12] Very recent results for the limits of detection for iridium and ruthenium in rhodium sponge using a d.c. arc on an Ebert 3-m spectrograph are 10 and 1 μg g^{-1}, respectively. The atomic-absorption spectrophotometric method gives similar sensitivity.

We are indebted to the University of Riyadh, Saudi Arabia, for a maintenance grant for M. A. Ashy and to Johnson Matthey Chemicals Ltd. for the loan of Specpure noble metals and rhodium sponge samples. We also thank Johnson Matthey Chemicals Ltd. for allowing us to use their Unicam SP1900 atomic-absorption spectrophotometer and for providing us with information on the detection limits for noble metals in rhodium sponge when carrying out emission spectrography.

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AN INDUCTION FURNACE FOR THE DETERMINATION OF CADMIUM IN SOLUTIONS AND ZINC-BASE METALS BY ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—An induction furnace coupled to a Unicam SP90 atomic-absorption spectrophotometer is described for the determination of traces of volatile elements in solutions and volatile matrices. The apparatus has been used to obtain calibration graphs for 1–20 and 50–750 ng of cadmium in μl-volumes of solution, the 228·8 and 326·2-nm resonance lines respectively being used, and to determine cadmium in 5-mg samples of zinc-base metals within the concentration range 5–400 μg/g by using the less sensitive 326·2-nm line. A furnace temperature of 1350° was used. Data on accuracy and precision are presented. The apparatus could readily be used to determine trace elements in volatile materials at concentrations of 10–1000 ng/g.

AS ATOMIC-ABSORPTION SPECTROSCOPY with flames has become very widely used in recent years, interest in non-flame methods of atomization has also increased. The principal advantages of non-flame methods over flame methods are that they are more sensitive, they can be used for very small volumes of solution and they can be employed to analyse small samples of solid material directly. Most published papers on non-flame methods have dealt with the analysis of materials originally in solution, the chief investigators in this field being L'vov,[1] Massmann,[2] West[3] and Woodriff.[4] Fewer results on the direct analysis of solid samples have been reported, but L'vov,[5] and Nikolaev[6] have analysed mg samples of metals, using an a.c. resistance furnace and the introduction of samples into the furnace on depressions in carbon rods. These methods are very sensitive, 10^{-5}% of impurity element being readily determined. Their precision is usually about 5–8%.

The present authors report the construction of a simple induction furnace to produce vapour from readily volatile elements, and the investigation of an atomic-absorption method using the furnace for the determination of cadmium in standardized zinc-base metals. An induction furnace was employed because many metallurgical firms already possess induction generators for the vacuum fusion of alloys. For comparison, some results are also reported for the analysis of μl samples of cadmium solutions.

EXPERIMENTAL

Apparatus

A diagram of the furnance is shown in Fig. 1. The central core consisted of a cylinder of graphite (Acheson E.G.W. grade) 75 mm long with internal diameter 15 mm and external diameter 38 mm. This cylinder rested in shaped firebrick cylinders, which in turn were situated in a recrystallized alumina tube (Thermal Syndicate Ltd.) which was 300 mm long with external diameter 54 mm and wall thickness of 4 mm. A hole of diameter 10 mm was drilled through the alumina tube and graphite cylinder such that a graphite rod (Le Carbone (G.B.) Ltd., grade 5501) shaped as shown could be raised from below until the tapered portion of the rod came in contact with the alumina cylinder. In this position the top of the rod was level with the bottom inside boundary of the graphite cylinder. An induction coil of six turns was wound around the alumina tube as shown. This coil was connected to a 6-kW Radyne Induction Generator.

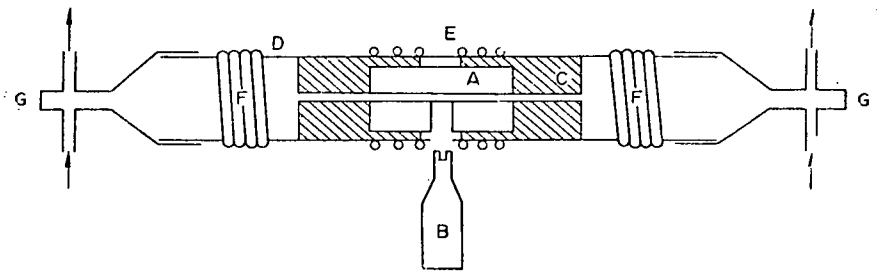

FIG. 1.—Graphite furnace for production of atomic vapour.
A—Graphite core; *B*—graphite electrode; *C*—firebrick packing; *D*—alumina tube; *E*—induction coil; *F*—cooling coils; *G*—Spectrosil windows.

End-pieces of Pyrex glass shaped as illustrated were constructed so that they slid smoothly over the ends of the alumina tube. These were sealed to the tube with Plasticine. Two cooling coils made from copper tubing of external diameter 6 mm were fixed near the ends of the alumina tube. The Pyrex end-pieces had Spectrosil windows (diameter 25 mm) fitted at their outer ends. Each end-piece had an inlet tube and an outlet tube for argon, each fitted with a tap. The inlet tubes were connected through a Y-piece to a flowmeter and a cylinder of argon.

Atomic-absorption measurements were made with the Unicam SP90, using a cadmium electrodeless discharge tube in a ¾-wave cavity powered by a Microtron 200 microwave generator fitted with a voltage stabilizing unit. When the discharge tube was used the lamp holder for hollow-cathode lamps was removed. Since the radiation from the discharge tube was not modulated electronically the SP90 was used in the emission mode, the light being modulated with a vibrating reed before striking the photomultiplier. A slit-width of 0·1 mm was used.

Determination of the absorbance of cadmium vapour in the furnace

Solutions. Flush all air from the furnace by opening the argon inlet tap at one end and the outlet tap at the other and passing argon at 12 l./min for about 5 min. Slowly raise the temperature of the furnace to 1350° by appropriate control of the Radyne Generator. A steady supply of 1·6 kW maintains this temperature. Adjust the controls on the Unicam SP90 so that a full-scale meter reading corresponds to 100% transmission.

Open the remaining two taps and reduce the argon flow-rate to 2 l./min. When the 228·8-nm cadmium line is used, place 10–50 µl of cadmium nitrate solution (cadmium 0·36 mg/l.) in the crater in the graphite rod and raise the rod into the furnace, at the same time shutting off the argon supply (Note 1). After a few seconds the transmission reading starts to fall and after 5–10 sec. reaches a steady value, which is maintained for about 5 sec. Note this transmission reading and from a conversion table read off the absorbance of the cloud of cadmium vapour. Then close the argon outlet tap at one end and the inlet tap at the other and flush out the cadmium vapour at a flow rate of 12 l./min for 2 min. Repeat the procedure as often as required.

Note 1. When the much less sensitive 326·2 nm cadmium line is employed, use 10–50 µl of cadmium nitrate solution (cadmium 7·1 mg/l.) in the crater.

Zinc-base metals. The procedure for metals is the same as for solutions except that 5 mg of metal is used in the crater and the less sensitive 326·2-nm cadmium line is employed. As for solutions the steady transmission reading for the cloud of metal vapour persists for approximately 5 sec.

Conventional determination of cadmium in the zinc-base metals

A 0·25 or 0·5-g sample of metal was dissolved in 5 ml of water plus 5 ml of concentrated hydrochloric acid. The solution was diluted to 25 ml in a graduated flask. The absorbances of these solutions were determined by using the air–acetylene flame of the Unicam SP90 and the 228·8-nm cadmium line. The calibration graphs were prepared from a series of 1% or 2% w/v zinc solutions containing 2–10 µg of cadmium per ml.

Some of the zinc-base metals were supplied by local industry and had been analysed by polarography. The polarographic results and the atomic-absorption spectroscopic results were in good agreement.

RESULTS

Calibration graphs for solutions of cadmium nitrate with the 228·8 and 326·2-nm lines are shown in Figs. 2 and 3 (curve A) respectively. The average absorbance from six aliquots of cadmium solution containing 8·9 ng of cadmium was 0·55 with a

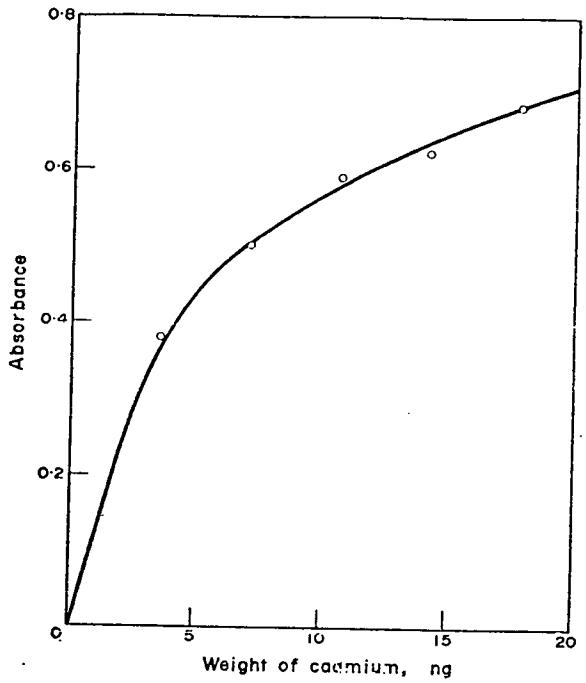

FIG. 2.—Calibration graph for determination of cadmium in solution, using the Cd 228·8-nm resonance line.

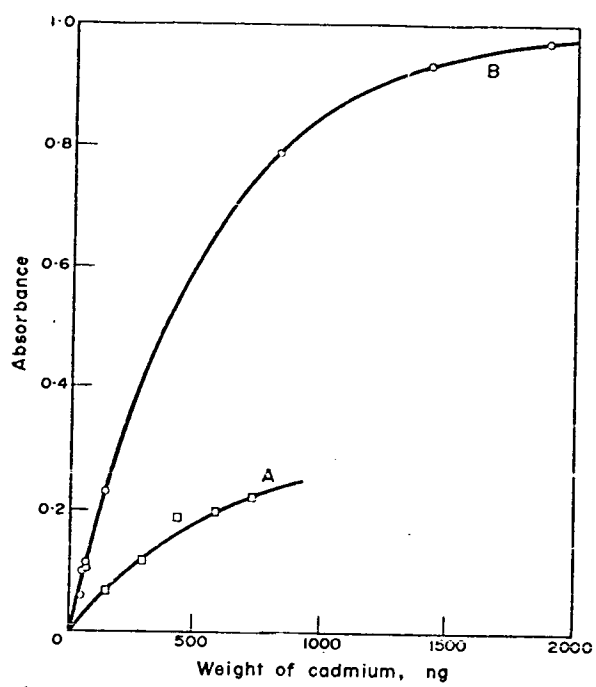

FIG. 3.—Calibration graphs for determination of cadmium in solution (A) and zinc-base metals (B), using the Cd 326·2 nm resonance line.

relative standard deviation of 6·4% (228·8-nm line) The average absorbance from six aliquots of cadmium solution containing 0·36 μg of cadmium was 0·14 with a relative standard deviation of 9·8% (326·2-nm line).

A calibration graph for the determination of cadmium in zinc-base metals is shown in Fig. 3, curve B. This was prepared by using eight of the metal samples that had been analysed by the conventional atomic-absorption spectroscopic method described above. The metals and their cadmium contents are shown in Table I. Alloy 24 was not used in the preparation of this calibration graph.

TABLE I.—THE CADMIUM CONTENTS OF THE ZINC-BASE METALS USED IN THIS STUDY

Metal	Cadmium content, μg/g
"Specpure" zinc (Johnson and Matthey)	8
Zinc powder (Koch-Light)	10
Granulated zinc (British Drug Houses)	12
Zinc shot (AnalaR, Hopkin and Williams)	13
Alloy 24	27
Alloy 17	28
Zinc needles (Prestons)	163
Zinc metal dust (Hopkin and Williams)	284
Zinc metal powder (Hopkin and Williams)	377

Absorbances for eight 5-mg samples of Alloy 24 were obtained during the run used to obtain absorbances for the calibration graph B in Fig. 3. The average absorbance for these samples was 0·22 with a relative standard deviation of 6·9%. The average cadmium content of this alloy, obtained by the furnace technique, was 26 μg/g compared with 27 μg/g by conventional atomic-absorption spectroscopy.

DISCUSSION

The results for the zinc-base metals are considered to be satisfactory. The relative standard deviation of 6·9% is appreciably larger than the standard deviations obtained with conventional atomic-absorption spectroscopy but part of this scatter will result from weighing errors, for the weight of a 5-mg sample could be in error by 0·2 mg, since only a four-place balance was used in this study. Also, when samples of only 5 mg are used, some scatter in the results can be expected from the distribution of cadmium not being completely homogeneous. The precision of 6·9% is also in good agreement with values of 5–8% obtained by L'vov.[1]

The method is quite rapid, for a 5-mg sample of metal can be analysed every 5 min. It must be noted that it is only possible to compare the furnace method with the conventional atomic-absorption spectroscopic method because a much less sensitive cadmium line at 326·2 nm is available. The furnace method using the 228·8-nm line is much too sensitive for the analysis of parts per million of cadmium in materials. However, the method should be especially useful for the determination of concentrations of cadmium at the ng/g level in volatile materials. An assessment of the quality of results for the determination of such concentrations of cadmium in volatile metals could not be made in this study for no standardized samples containing so little cadmium were available. The relative standard deviation of 6·4% obtained for the cadmium nitrate solutions, the 228·8 nm line being used, does indicate, however, that ng/g concentrations of cadmium in solid materials should be capable of determination with similar precision.

The 1% absorption values for the determination of cadmium in solutions and zinc-base metals are 24 pg (228·8 nm), and 9·7 ng (326·2 nm), and 2·3 ng respectively. For zinc-base metals this corresponds to 0·46 μg/g for a 5-mg sample. It will be seen that for solutions the method is 400 times more sensitive with the 228·8 nm line than with the 326·2 nm line. Therefore it can be expected that for zinc-base metals, the 1% absorption value for the 228·8-nm cadmium line will be about 1 ng/g.

It will be observed from Fig. 3 that the calibration graph for the 326·2 nm line has a lower slope for solutions than that for zinc-base metals.

For solutions, interfering effects are to be expected from other ions, particularly anions, since it is likely that many molecular cadmium species will not be completely dissociated at 1350°.

Since a transmission reading steady for approximately 5 sec is obtained after the introduction of a metal sample, it seems unlikely that during this period, there are any solid particles or liquid globules in the light-path, which could scatter light. Therefore interfering effects caused by scattering are considered to be unlikely. As the furnace is operated in a pure argon atmosphere there should be little interference from molecular species in the light-path when zinc samples are analysed for cadmium.

The maximum temperature of operation of the furnace is 1900°. An induction furnace is now being built for the analysis of less volatile alloys at 2500–3000°.

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Zusammenfassung—Ein an ein Unicam SP 90 Atomabsorptions-Spektrophotometer gekoppelter Induktionsofen wird beschrieben; er wird Bestimmung von Spuren flüchtiger Elemente in Lösungen und flüchtigen Matrizen eingesetzt. Das Gerät wurde zur Aufnahme von Eichkurven für 1–20 und 50–750 ng Cadmium in μl-Lösungsvolumina verwendet, wobei die Resonanzlinien bei 228,8 bzw. 326,2 nm benutzt wurden, sowie zur Bestimmung von Cadmium in 5 mg-Proben von Metallen mit Zink als Hauptbestandteil, im Konzentrationsbereich 5–400 μg/g, unter Verwendung der weniger empfindlichen Linie bei 326,2 nm. Der Ofen wurde auf 1350° gehalten. Genauigkeits- und Richtigkeitsdaten werden mitgeteilt. Das Gerät konnte zur Bestimmung von Spuren in flüchtigem Material bei Konzentrationen von 10–1000 ng/g gut verwendet werden.

Résumé—On décrit un four à induction couplé à un spectrophotomètre d'absorption atomique Unicam SP 90 pour le dosage de traces d'éléments volatils en solution et dans des matrices volatiles. L'appareil a été utilisé pour obtenir des courbes d'étalonnage pour 1–20 et 50–750 ng de cadmium dans des μl de solution, les raies de résonance 228,8 et 326,2 nm étant respectivement utilisées, et pour doser le cadmium dans des échantillons de 5 mg de métaux à base de zinc dans le domaine de concentration 5–400 μg/g en utilisant la raie moins sensible 326,2 nm. On a utilisé une température de four de 1350°. On présente des données sur la précision et la fidélité. On peut aisément utiliser l'appareil pour déterminer des éléments à l'état de traces dans des substances volatiles à des concentrations de 10–1000 ng/g.

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DETERMINATION OF TRACE ELEMENTS IN METALS AND ALLOYS BY ATOMIC-ABSORPTION SPECTROSCOPY USING AN INDUCTION-HEATED GRAPHITE WELL FURNACE AS ATOM SOURCE

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Summary—An induction-heated graphite furnace, coupled to a Unicam SP 90 atomic-absorption spectrometer, is described for the direct determination of trace elements in metals and alloys. The furnace is capable of operation at temperatures up to 2400°, and has been used to obtain calibration graphs for the determination of ppm quantities of bismuth in lead-base alloys, cast irons and stainless steels, and for the determination of cadmium at the ppm level in zinc-base alloys. Milligram samples of the alloys were atomized directly. Calibration graphs for the determination of the elements in solutions were obtained for comparison. The accuracy and precision of the determination are presented and discussed.

IN RECENT years much interest has been shown in the development of non-flame methods of atomization for atomic-absorption spectroscopy.[1] Many such atomization methods have been reported but few have dealt with systems suitable for direct analysis of solid samples. The authors have previously reported on an induction furnace for the direct determination of trace elements by atomic-absorption spectroscopy using the solid sample directly.[2] The results obtained were very encouraging and it was decided that further investigations on a similar atomizer should be continued. The major disadvantage of the system described previously was that, since alumina sheathing was used, the operating temperature was limited to approximately 1900°. A furnace, based on a system commonly used for vacuum fusion, and capable of operation up to 2400°, was thus constructed, and the application of this furnace to atomic-absorption spectroscopic determination of trace elements is reported.

EXPERIMENTAL

Apparatus

A diagram of the furnace is shown in Fig. 1. The carbon core consisted of a cylinder of graphite, 120 mm long and 38 mm in diameter, with a 13 mm hole bored centrally along its length to within 10 mm of one end. Light-guides, consisting of graphite tubes 75 mm long, 15 mm outside diameter and with a 6 mm bore, were positioned at each side of the core, centred on a point 50 mm from the base (closed end). Acheson e.g.w. grade graphite was used in this construction.

The core was held in a quartz tube, 130 mm long and 47 mm internal diameter, with side-arms, 50 mm long and 18 mm internal diameter to cover the light-guides. The side-arms were tapered at their ends to give a tight fit on the light-guides. The space between the graphite core and quartz sheathing was packed with insulating graphite, 300 mesh.

The core was heated by a six-turn induction coil wound round the quartz sheathing as shown in the diagram, the power to the coil being supplied by a 6 kW Radyne Induction Generator.

The whole of this was seated on an asbestos work-table and enclosed by an asbestos box which was sealed to the table with refractory cement. The box had gas inlet and outlet points so that the system could be flushed out and operated in an inert gas atmosphere. Argon was used in these experiments. "Spectrosil" windows, 40 mm in diameter, were fitted in two sides of the asbestos box, in line with the light-guides to allow the passage of light through the cell.

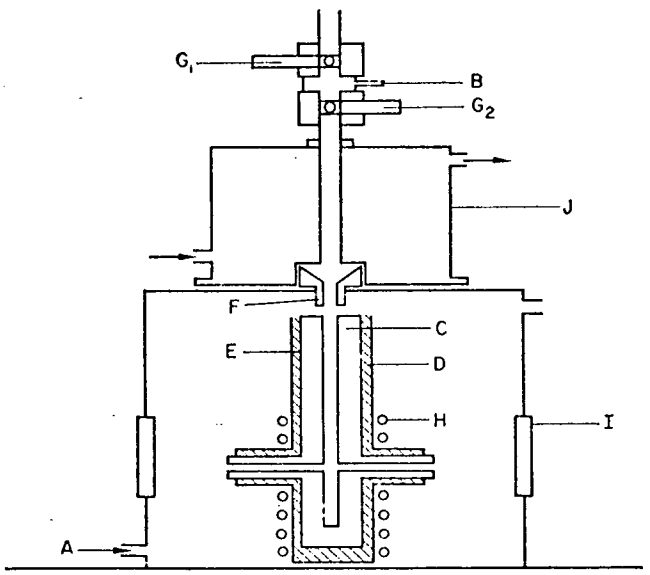

FIG. 1.—Induction-heated graphite furnace for atomic-absorption spectroscopy. *A*, Argon inlet; *B*, argon inlet; *C*, graphite core; *D*, quartz sheath; *E*, graphite insulation; *F*, graphite funnel; G_1 and G_2, Econ-O-Miser ball valves type 44/46/T (Worcester Valve Co. Ltd.) of 13-mm nominal bore; *H*, induction coil; *I*, "Spectrosil" windows; *J*, aluminium cooling jacket with cold water circulating through it.

Samples were introduced into the furnace from above *via* a double valve arrangement which prevented the introduction of air along with the sample. A graphite funnel was positioned in the top of the asbestos box, directly above the bore in the graphite core, to guide the samples into the hot core. A hollow aluminium cooling unit was designed to fit under the valves and over the graphite funnel, and was secured to the lid of the asbestos box. This was necessary to prevent heat from the furnace destroying the Teflon valve seats and seals.

Radiation was provided by electrodeless discharge tubes. These were powered by a Microtron 200 microwave generator, fitted with a voltage stabilizing unit and frequency modulator unit operating at 50 Hz. A Unicam SP 90 atomic-absorption spectrophotometer was used as detector and amplification unit, the output signal being obtained on a Honeywell 10 mV recorder, fast-response type.

Preliminary investigations

To obtain maximum sensitivity of the atomic-absorption determination when using a system such as that described above, it is necessary, particularly when a peak-height method of absorbance measurement is used, that all the atoms of the element of interest appear in the light-path in a short period of time. Thus when solid samples were used, sensitivity was expected to be dependent upon the furnace temperature, and preliminary experiments were carried out to investigate this point. These indicated that the optimum temperature is one just above the boiling point of the matrix element, provided the element of interest is also volatile at this temperature.

Should the element to be determined be less volatile than the matrix element, a temperature just above the boiling point of the trace element should be used. When the matrix element is not in the gaseous phase at the maximum temperature of the furnace, suitable calibration graphs can still be obtained provided that the matrix element is molten and the element of interest is volatile.

A similar series of experiments was carried out to investigate the effect of varying the argon gas flow. Maximum sensitivity was obtained when the argon flow was stopped just before introduction of the sample into the furnace, the flow being restored after the peak, to flush metal vapour from the cell.

General procedure

The argon flow through inlet *A* was adjusted to 10 l./min to flush out the system. The Radyne generator was adjusted to bring the furnace to a suitable temperature and the argon flow was adjusted to 7 l. min. Valve G_1 was opened and a sample was introduced into the sample tube (see Note).

Argon inlet *B* was opened and a flow of 2 l. min was used to flush out air from the sample tube. Valve G_1 and argon inlet *B* were then closed.

The controls of the SP 90 were adjusted to give a transmission setting of 100% on the recorder. The argon supply was stopped by closing argon inlet *A*, and valve G_2 was opened and closed quickly to allow the sample to fall into the "well" furnace. After recording of a minimum transmission reading, argon inlet *A* was opened and an argon flow of 7 l. min was used to flush out the system.

Once the base-line for 100% transmission had again been achieved, the procedure was repeated for the next sample.

Note. In analysis for trace elements directly on solid samples, small pieces of the materials under study (mg samples) were introduced into the furnace. These materials were alloys which contained traces of elements of which the concentrations had been determined by well-established analytical methods. For solution analysis, small volumes were dispensed by micrometer syringe and were collected on carbon pellets 6 mm in diameter and 3 mm in depth. After evaporation of the solvent, to produce a solid deposit of the salt, the carbon pellets were added to the furnace as described above. Standard solutions of the metals were prepared by dissolving the metals in nitric acid.

RESULTS

Calibration graphs for the determination of cadmium in zinc-base alloys (curve *A*) and solutions (curve *B*), using the 228·8-nm line and furnace temperatures of 1050° and 2300° respectively are shown in Fig. 2. A temperature of 2300° was used to ensure dissociation of any molecular species of cadmium formed from cadmium nitrate. The sensitivities (1% absorption values) calculated from these graphs were 0·40 ng for cadmium from zinc-base alloys and 0·62 ng for cadmium from solution. As 5-mg samples of zinc-base alloys were used, the 1% absorption value for cadmium in zinc-base alloys corresponds to a concentration of 0·08 μg/g.

Calibration graphs for the determination of bismuth in lead-base alloys, stainless steels, cast irons and solutions are shown in Figs. 3 and 4 respectively. The resonance

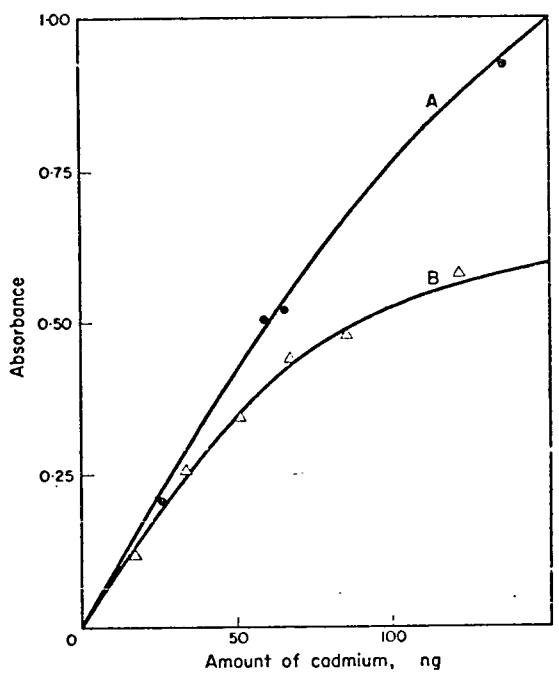

FIG. 2.—Calibration graphs for the determination of cadmium in (*A*) zinc-base alloys and (*B*) solutions.

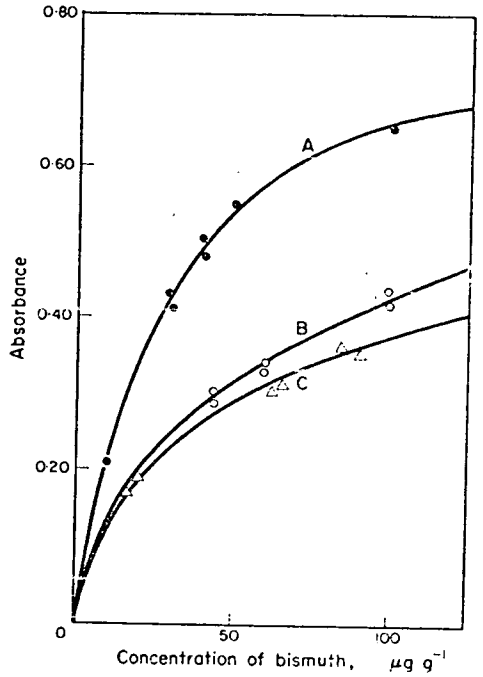

FIG. 3.—Calibration graphs for the determination of bismuth in (*A*) lead-base alloys; (*B*) stainless steels and (*C*) cast irons.

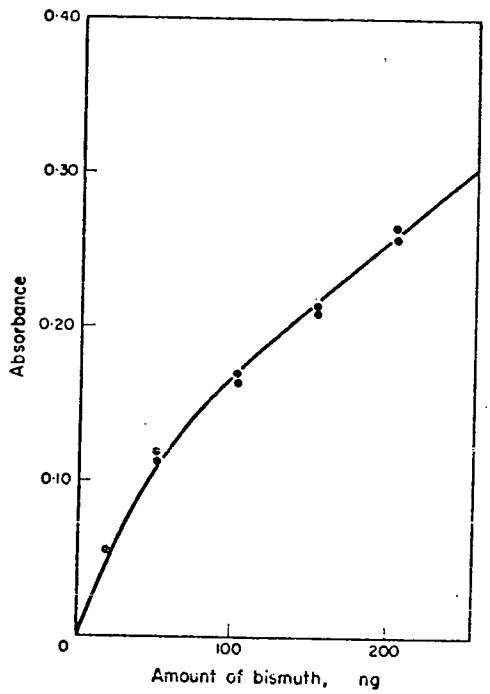

FIG. 4.—Calibration graph for the determination of bismuth in solution.

line at 306·8 nm was used in all cases. A furnace temperature of 1775° was employed for the lead-base alloys, all other determinations being carried out at 2400°. All the graphs in Fig. 3 have been obtained for solid samples and the abscissa conveniently shows the concentration of bismuth (μg/g) in the 6-mg samples used. The 1% absorption values calculated from the calibration graphs were 0·24 μg/g for bismuth from lead-base alloys, 0·30 μg/g for bismuth from stainless steels and 0·33 μg/g for bismuth from cast irons. Since the weights of sample used were 6 mg, these 1% absorption values correspond to amounts of bismuth of 1·4 ng for lead-base alloys, 1·8 ng for stainless steels and 2·0 ng for cast irons. By comparison the 1% absorption value for bismuth from solution, calculated from Fig. 4, was 1·4 ng.

Accuracy and precision data obtained for the determination of bismuth in lead-base alloys and cast irons, together with corresponding figures for the determination of cadmium in zinc-base alloys are summarized in Table I. In order to obtain these results, a sample of the appropriate alloy, not used in the preparation of the calibration graph, was analysed a number of times by the procedure given, the concentrations being read off the calibration graph.

TABLE I.—ACCURACY AND PRECISION OF ANALYSES USING GRAPHITE INDUCTION FURNACE

Determination	No. of samples analysed	Concentration of trace element determined $\mu g/g$		Relative standard deviation %
		This method	Independent method	
Bi in lead-base alloy	10	43	40	8·1
Bi in cast iron	10	66	63	8·1
Cd in zinc-base alloy	6	12·7	13·0	3·6*

* These samples were weighed on a semimicro 5-place balance; other samples were weighed on a 4-place laboratory balance.

DISCUSSION

The results obtained for the determination of bismuth and cadmium in various matrices were considered to be satisfactory, the accuracy and precision of the determinations using the graphite "well" furnace being quite comparable with those obtained by other workers on furnace systems. As indicated in Table I, weighing errors can account for a considerable proportion of the error and, if more sensitive balances are used, the precision can be improved.

All the calibration graphs are curved, and this is thought to be due mainly to a sluggish response of the amplification system to a rapidly changing signal. This becomes particularly noticeable when a peak-height method of absorbance measurement is used. Since distortion of the peak height will increase as the height of the peak increases, curved calibration graphs result.

The decrease in sensitivity of bismuth determination from lead-base alloys to cast irons and stainless steels is due to the use of a peak-height method of absorbance measurement. Since the maximum temperature available was not above the boiling point of the base element in the last two types of sample, vaporization of the trace element of interest was not so rapid. The absorption peaks were shallower and broader than those obtained with the more volatile base materials. Use of an integration method of absorbance measurement would probably overcome this lack of sensitivity.

Although the sensitivities obtained by using the graphite "well" furnace are not so good as those obtained with the horizontal furnace described previously,[2] it is felt that this furnace does have a future. It appears particularly useful for the determination of trace elements at the ppm level, using the solid sample directly.

Initial determinations of tin at the ppm level in lead-base alloys and aluminium-base alloys have also been carried out successfully. The furnace appears suitable for the determination of many elements, including Ag, As, Ca, Hg, Mg, Mn, Pb, Sb and Zn, in a wide range of matrices. Whilst the accuracy and precision values so far obtained by this technique may not be acceptable for the most exacting determinations at the ppm level, the technique could prove very useful as an analytical tool for rapid semi-quantitative analysis.

Acknowledgements—One of the authors (D. R. S.) thanks the Science Research Council for a Studentship to undertake this work. The authors are indebted to B.I.S.R.A. and B.C.I.R.A. for provision of samples and to Mr. W. R. Nall of Bragg Laboratory, Sheffield for discussion in connection with certain samples.

Zusammenfassung—Ein an ein Unicam SP 90-Atomabsorptionsspektrometer gekoppelter Graphit-Induktionsofen wird beschrieben, der zur direkten Bestimmung von Spurenelementen in Metallen und Legierungen dient. Der Ofen kann bei Temperaturen bis 2400° betrieben werden und wurde verwendet zur Aufstellung von Eichkurven zur Bestimmung von ppm-Mengen Wismut in Legierungen mit Blei als Grundmetall und zur Bestimmung von Cadmium im ppm-Bereich in Legierungen auf Zinkbasis. Milligramm-Proben der Legierungen wurden direkt in den atomaren Zustand überführt. Zum Vergleich wurden Eichkurven zur Bestimmung der Elemente in Lösung aufgenommen. Genauigkeit und Richtigkeit der Bestimmung werden angegeben un diskutiert.

Résumé—On décrit un four de graphite chauffé par induction et couplé à un spectromètre d'absorption atomique Unicam SP 90 pour le dosage direct de traces d'éléments dans les métaux et alliages. Le four est capable d'opérer à des températures allant jusau'á 2400°, et a été utilisé pour obtenir des courbes d'étalonnage pour le dosage de quantités de l'ordre du ppm de bismuth dans des alliages à base de plomb, des fontes et des aciers inoxydables, et pour le dosage du cadmium au niveau de la ppm dans des alliages à base de zinc. Des échantillons des alliages, de l'ordre du milligramme, ont été atomisés directement. Les courbes d'étalonnage pour le dosage des éléments en solutions ont été obtenues pour comparaison. On présente la précision et la fidélité du dosage et en discute.

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DETERMINATION OF TRACE AND MINOR ELEMENTS IN ALLOYS BY ATOMIC-ABSORPTION SPECTROSCOPY USING AN INDUCTION-HEATED GRAPHITE-WELL FURNACE AS ATOM SOURCE—II*

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An induction-heated graphite-well furnace used in conjunction with electrodeless discharge tubes as light-sources and the monochromator and detector of a Unicam SP90 atomic absorption spectrophotometer, has already been described for the determination of ppm quantities of bismuth in lead–base alloys, cast irons and stainless steels, and for the determination of cadmium at the ppm level in zinc–base alloys. Small samples of alloy, 5 or 6 mg in weight, were dropped into the furnace for these determinations. In this communication some further results are presented for the determination of zinc in aluminium and aluminium–silicon alloys and of aluminium, antimony and tin in steels.

EXPERIMENTAL

Apparatus

The apparatus has already been described in detail.[1] Temperatures were measured with a Land Disappearing Filament Pyrometer Type DFP 2C by looking down through the open valves into the base of the furnace. Temperatures could be measured with an accuracy of ± 10°C but are not corrected for the emissivity value of graphite

* Part I: J. B. Headridge and David Risson Smith, *Talanta*, 1972, **19**, 833.

(0·90). The measured temperatures will be slightly lower than the true temperatures with an estimated maximum error of 35°C at 2500°C.

Electrodeless discharge tubes were made in the laboratory according to well-known procedures.[2–4]

Procedure

Use as a light-source either an electrodeless discharge tube or a hollow-cathode lamp of the element to be determined in the alloy samples. Weigh out 5 or 10 mg of standard alloys (similar to the samples) and the alloys to be analysed for the trace or minor element. Drop these samples consecutively into the furnace as described in the previous paper, measuring the absorbance of the vapour cloud for each sample. Construct a calibration graph for the standard samples and use this graph to determine the concentration of trace or minor element in the samples. If the rather tedious procedure of weighing 5 mg samples all to the nearest 0·1 mg is used, the abscissa of the calibration graph is "Concentration of the trace element". However it is easier to weigh out the samples accurately to the nearest 0·1 mg. but ensuring that their weights fall within the range of 4·5 to 5·5 mg, and to make simple calculations such that the abscissa reads "Weight of the trace element." Slight differences in the weights of samples do not appear to lead to any decrease in accuracy or precision for a determination.

Alloy samples

The alloys used for the construction of the calibration graphs, with the concentrations of minor or trace elements in parentheses, and the furnace temperatures, are shown in Table 1.

Samples weighing 5 mg were used throughout except for the calibration graph for zinc in aluminium alloys, where 10 mg samples were employed.

Table 1. Alloys and temperatures used for caibration graphs

Determination	Alloys used (concentrations in %)	Temperature, °C
Zn in Al alloys	BCS 268(0·05), BCS 181/2(0·07) BCS 182/2(0·10), BCS 216/2(0·20)	2350
Zn in Al-Si alloys	SS 504(0·06), SS 502(0·21), SS 505(0·24)	2350
Al in steels	BCS 320(0·013), BCS 327(0·020), BCS 325 (0·028), BCS 329(0·058), BCS 322(0·093)	2450
Sb in steels	BCS 325(0·002), BCS 326(0·005), BCS 329(0·018), BCS 328(0·026)	2400
Sn in steels	BCS 321(0·014), BCS 323(0·024), BCS 218/3(0·042), BCS 325(0·046), BCS 320(0·085)	2400

RESULTS AND DISCUSSION

Suitable calibration graphs were obtained for zinc in aluminium and aluminium–silicon alloys, and aluminium, antimony and tin in steels. They all had convex curvature except that for tin, which was linear. Alloys SS 503, BCS 328, BCS 330 and BCS 239/3 were analysed eight, ten, eight and seven times respectively for the accuracy and precision data shown in Table 2.

The amounts and concentrations of these elements in their respective matrices required to give 1% absorption when heated in the induction furnace, as calculated from the calibration graphs, are shown in Table 3.

Table 2. Accuracy and precision of analyses

Determination	Line, *nm*	Relative standard deviation, %	Content by this method, %	Content by independent method, %
Zn in Al–Si alloy*	307·6	4·2	0·148	0·15
Al in mild steel	309·3	7·1	0·046	0·048
Sb in mild steel	231·1	7·4	0·017	0·018
Sn in steel	284·0 / 286·3	9·4	0·032	0·030

* The less-sensitive resonance line for zinc was used.

Table 3. Amounts and concentrations of elements required for 1% absorption

Element	Matrix	Amount, *ng*	Concentration for 5-mg sample, *μg/g*
Zinc	Al-base	60	12
Aluminium	Mild steel	25	5
Antimony	Mild steel	4	0·8
Tin	Steel	50	10

The accuracy of the results is satisfactory, as can be seen from Table 2, provided that the compositions of the standards and the samples to be analysed are similar. This restriction also applies to certain other analytical methods using solid samples, such as emission spectrography and X-ray fluorescence spectroscopy. An incorrect result for the determination of the minor or trace element in a sample can be obtained if the sample contains a high concentration of another volatile element, compared with the standards. For example, the aluminium alloys BCS 268 (used in the construction of the calibration graph) and BCS 262 each contain 0·05% of zinc but 0·56% and 10·57% of magnesium respectively. Magnesium is a volatile element boiling at 1107°. The absorbance for zinc for BCS 262 is considerably greater than that for BCS 268, indicating that the volatile magnesium in high concentration sweeps out the zinc from the matrix more readily with BCS 262 and leads to a higher peak concentration of zinc in the vapour cloud. An examination of the concentrations of major elements in alloys along with their boiling points will show if any interference effects might be expected.

The precision of the results is similar to that obtained by other workers using non-flame methods of atomization. The precision should be improved if a semimicro balance is used to weigh the samples.[1] The sensitivity of the method for zinc will be greatly increased by using the more sensitive resonance line at 213·9 nm. However, no suitable alloy samples of sufficiently low zinc content were available for the construction of a calibration graph using this line. The sensitivities of the method for the determination of aluminium, antimony and tin in steels will be improved if the temperature of the furnace can be raised by several hundred degrees. The maximum temperature of the furnace was 2500°C but iron boils at 3000°C and the results from the previous study[1] showed that the best sensitivity is obtained at a temperature just above the boiling point of the base element when the element to be determined is more volatile.

By use of aqueous salt solutions dispensed onto carbon or tungsten discs, suitable calibration graphs were also obtained for lead, magnesium, manganese and silver, the amounts for 1% absorption being 4, 0·03, 1·4 and 0·1 ng respectively. It should also be possible to determine trace amounts of these elements in alloys if suitable standards are available.

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Summary—Results are presented for the atomic-absorption spectrophotometric determination of zinc in aluminium and aluminium–silicon alloys, and aluminium, antimony and tin in steels, by means of solid samples dropped into an induction-heated graphite-well furnace to produce the atomic vapour.

Zusammenfassung—Es werden Ergebnisse von atomabsorptionsspektrophotometrischen Bestimmungen von Zink in Aluminium und Aluminium–Silicium–Legierungen sowie von Aluminium, Antimon und Zinn in Stählen mitgeteilt. Dabei werden zur Erzeugung des atomhaltigen Dampfes die festen Proben in einen induktiv geheizten Graphit-Schachtofen fallen gelassen.

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Determination of Bismuth in Steels and Cast Irons by Atomic-absorption Spectrophotometry with an Induction Furnace: Direct Analysis of Solid Samples

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A graphite induction furnace has been constructed within a Perkin-Elmer 300S atomic-absorption spectrophotometer for the determination of bismuth in 2–12-mg samples of steels and irons that are dropped into the furnace. Calibration graphs of peak absorbance *versus* mass of bismuth are best constructed by use of standard alloys of roughly similar composition to the samples being analysed but, in the absence of suitable standard alloys, semi-quantitative results can be obtained if calibration graphs are prepared using small volumes of a standard bismuth nitrate solution.

Samples of alloys can be added to the furnace at 2–5-min intervals. Information is presented on the calibration graphs and on the accuracy, precision and limits of detection of the method for 40 high-purity irons and steels and for nine cast irons. With steels containing more than 0.04 $\mu g\ g^{-1}$ of bismuth, relative standard deviations of 3–10% are usually achieved. The limit of detection for bismuth in steels is 0.004 $\mu g\ g^{-1}$ when using this method.

Keywords: Bismuth determination; steel and cast iron analysis; atomic-absorption spectrophotometry; induction furnace; direct analysis of solids

An element present in very low concentrations will have no appreciable effect on the mechanical properties of a metal provided that it is uniformly distributed throughout the material. However, if certain elements are confined to dislocations or grain boundaries, they can exert profound effects on the properties of metals when present even at concentrations less than 0.001% (10 $\mu g\ g^{-1}$).[1] For example, concentrations of tin well below 1 $\mu g\ g^{-1}$ affect the rate of grain boundary migration in lead[2] and for nickel-alloy castings the SAE Aerospace Materials Specification 2280 lists maximum concentrations of certain trace elements, *viz.*, bismuth and tellurium, 0.5 $\mu g\ g^{-1}$, selenium, 3 $\mu g\ g^{-1}$, and lead and thallium, 5 $\mu g\ g^{-1}$.[3]

The metallurgist is particularly interested in knowing the concentration levels at which troublesome elements cease to impair the properties of alloys, but he is sometimes prevented from obtaining this information through research because the analyst is unable to determine such elements at the lowest concentration levels required. This inability arises because the limits of detection of the analytical methods are not good enough.

As long ago as 1961 Lynch[4] suggested that the maximum concentration of bismuth in Type 300 austenitic steel should be 10 $\mu g\ g^{-1}$ if hot embrittlement was to be avoided, and the problem of determining very low concentrations of bismuth in steels has received considerable attention since then.[5–9] The lowest reported limit of detection for bismuth in steels appears to be 0.2 $\mu g\ g^{-1}$,[5] although a limit of detection of 0.1 $\mu g\ g^{-1}$ has been reported for bismuth in nickel-base and high-temperature alloys.[10,11] However, if the metallurgist is to be given the maximum flexibility in his investigations it would be desirable to lower this limit of detection to 0.01 $\mu g\ g^{-1}$. At such low concentrations of bismuth, the amount of bismuth in a solution blank can be in excess of the amount of bismuth from a sample of steel dissolved in the solution and, therefore, a direct analysis of the metal sample without dissolution is to be preferred.

Headridge[12] described an induction furnace in conjunction with atomic-absorption spectrophotometry for the determination of trace elements in alloys. In this method solid samples of alloys were dropped into the furnace. For a 5-mg sample of cast iron, the concentration of bismuth that would produce 1% absorption was 0.4 $\mu g\ g^{-1}$. The Unicam SP90 atomic-absorption spectrophotometer used in that study was not ideally suited to the project and many improvements in the method have been made since the experiment was first described.

A re-designed furnace, used with a Perkin-Elmer 300S atomic-absorption spectrophotometer, has produced significantly better results and the limit of detection of bismuth in steels has been lowered to 0.004 $\mu g\ g^{-1}$. The new apparatus is described in this paper and results are presented for the determination of bismuth in 40 standard, high-purity irons and steels and in nine standardised cast irons.

Experimental

Materials

Standardised irons and steels. These were British Chemical Standards, alloys from the Institutet för Metallforskning, Sweden, cast irons from the British Cast Iron Research Association and four stainless steels from the British Steel Corporation.

Bismuth metal. Koch-Light Laboratories Ltd., 99.9995%.

Nitric acid. Fisons analytical reagent grade, sp. gr. 1.42.

Standard bismuth nitrate solution A (approximately 10 $\mu g\ cm^{-3}$). Weigh accurately, on a five-place balance, approximately 10 mg of bismuth. Dissolve the metal in 13 cm^3 of concentrated nitric acid and dilute the solution to 100 cm^3 in a calibrated flask. Immediately before use, dilute 10 cm^3 of this solution to 100 cm^3 in a calibrated flask with 2 M nitric acid.

Standard bismuth nitrate solution B (approximately 2.5 $\mu g\ cm^{-3}$). Immediately before use dilute 25 cm^3 of solution A to 100 cm^3 in a calibrated flask with 2 M nitric acid.

Graphite and carbon rods. The graphite rods were 525 mm long × 25 mm diameter and 900 mm long × 38 mm diameter in AGW grade graphite (British Acheson Electrodes). Specpure carbon was used to make rods 31 mm long × 6.5 mm diameter (supplied by Johnson Matthey Chemicals Ltd.).

Graphite powder. Natural graphite, 98–99%, obtained from Hopkin and Williams.

Copper tubing, 0.25 in *o.d.*

Vydaflex III sleeving, 6 mm *bore.*

Argon.

*BASF catalyst R*3–11. Before use regenerate the catalyst with hydrogen according to the manufacturer's instructions.

Apparatus

Atomic-absorption spectrophotometer. This was a Perkin-Elmer 300S instrument, equipped with a bismuth hollow-cathode lamp (Pye Unicam). The resonance lines at 306.8 and 227.7 nm were used with a slit-width of 0.2 nm. The output signal (absorbance) of the 300S, employed with minimum damping (position 1), was fed via a simple active noise filter to a 10-mV recorder (Honeywell Controls Ltd.). The noise filter damped minor signal fluctuations but did not affect the amplitudes of peak absorbances.

Induction generator. Radyne C50, 6-kW output, with a nominal output frequency of 450 kHz.

Optical pyrometer. Land disappearing filament pyrometer, Type DFP 2C. Temperatures could be measured with an accuracy of ± 10 °C but are not corrected for the emissivity value of graphite (0.90). The measured temperatures will be slightly lower than the true temperatures; the estimated maximum error is 35 °C at 2 500 °C.

Vibrator. Burgess Vibrotool engraver, Model No. VT62.

Flow meters. These instruments were capable of measuring 0–250 $cm^3\ min^{-1}$ [calibrated for air (Rotameter Mfg. Co. Ltd.)] and 0–10 $dm^3\ min^{-1}$ [calibrated for air (Flowbits)].

Furnace. This was constructed as is shown in Figs. 1 and 2. The central, vertical graphite rod was machined to produce a graphite well. Two holes were then drilled in the sides of the well at the correct height to accommodate the two short side-arms, which had been machined appropriately. The central graphite rod was inserted into a silica sheath of dimensions such as to allow a clearance of approximately 5 mm between the silica and the the graphite core. The graphite side-arms were then pushed through the side-arms of the silica sheath into the graphite core. They were a push-tight fit in the graphite core and a sliding fit in the silica side-arms. The copper tubing covered with Vydaflex sleeving was next wound around the silica sheath to give two turns above and four turns below the side-arms. Finally, the annular discs of graphite of push-tight fit were pushed on to the two ends of the graphite side-arm to abut against the ends of the silica. The space between the

graphite and the silica sheath was filled with graphite powder, using the vibrator to ensure an even packing.

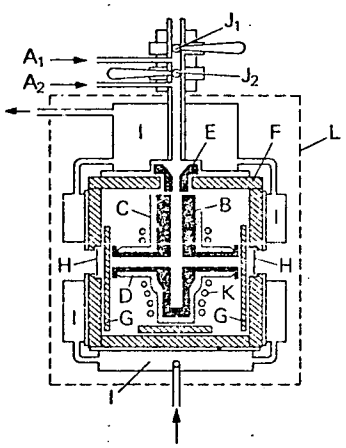

Fig. 1. Induction-heated graphite furnace for atomic-absorption spectroscopy. A_1, Argon inlet for purge gas from taps T_1 and T_2 (not shown in figure); A_2, argon inlet for stir gas; B, graphite core with side arms; C, silica sheath; D, graphite insulation; E, graphite funnel; F, Sindanyo box; G, shutter; H, silica window of diameter 40 mm; I, aluminium cooling panels through which cold water circulates (top and side panels are annular); J_1 and J_2, Econ-O-Miser ball valves, Type 44/46/T (Worcester Valve Co. Ltd.) of 13 mm nominal bore; K, induction coil; L, Faraday cage.

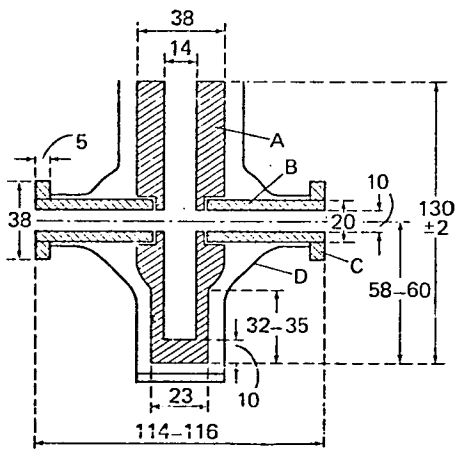

Fig. 2. Furnace core and silica sheath, including dimensions. A, Vertical graphite core; B, graphite side arm; C, annular graphite ring; D, silica sheath with thick silica base. All dimensions are in millimetres.

The Sindanyo box (a composite of asbestos and Portland cement) with water cooling panels was positioned on a shelf attached to the front of the Radyne generator such that the Perkin-Elmer 300S could be pushed into position on a trolley with the box in the large space normally occupied by the burner. The width of this space is 27.5 cm and it extends downwards from the top of the spectrophotometer for 22 cm. There is no restriction on access to this space from the front or the back of the instrument. The upper cooling panel and the valves, constructed as one unit, were removed followed by the Sindanyo lid. The silica sheath within the induction core was positioned in the Sindanyo box such that the light beam from the hollow-cathode lamp to the monochromator of the Perkin-Elmer 300S passed through the centre of the graphite side-arms. The well was checked to ensure that it was vertical. Next, the ends of the copper tubing, passing through slots in the back of the Sindanyo box, were attached to the induction generator, the Sindanyo lid was screwed back on to the box, the graphite funnel for directing samples into the vertical core was placed centrally on top of the core and the upper cooling panel, with the valves attached, was screwed into position on the Sindanyo lid.

The inlet tubes for argon gas were attached as is shown in Fig. 1. Argon destined for the inlet between the valves was passed through a simple tap T_1, through an absorption tube (40 cm long × 5 cm diameter) containing BASF catalyst in order to remove traces of oxygen, then through the 0–10 dm^3 min^{-1} flow meter and finally through a simple tap T_2 before use. Argon to be passed down the graphite core from the lower inlet tube was passed through an absorption tube (60 cm long × 5 cm diameter) containing BASF catalyst and through the 0–250 cm^3 min^{-1} flow meter before use. Argon passed into the graphite core escapes through

the side-arms into the Sindanyo box and hence through the slots at the back to the atmosphere.

When the furnace was in use, cold water from the public supply was circulated through the cooling panels in order to ensure that the temperature of the Perkin-Elmer 300S was not raised by the considerable amount of heat generated from the graphite core and also to keep the PTFE valve seats and seals cool. The furnace was also fitted with two Sindanyo shutters positioned inside the Sindanyo box. These shutters were usually pushed in, so that they lay between the side-arms and the silica windows. They were only pulled out of the light path when adjustments involving the beam were being made to the spectrophotometer and when a recording of an absorbance peak was required. Their function was to protect the hollow-cathode lamp, the lenses, the monochromator and the detector from excessive visible and infrared radiation and to minimise the deposition of very small metallic particles on the silica windows while the graphite core was being purged with argon. The furnace box was completely surrounded by a Faraday cage, which extended backwards to the front panel of the induction generator in order to ensure that the electronic components of the atomic-absorption spectrophotometer were unaffected by stray radiofrequency fields.

Method for Obtaining Absorbances for a Series of Solid Samples

Weigh 2–12 mg samples of steels or cast irons by using a five-place semi-micro balance and store them in small specimen tubes. If possible, weigh only one turning of the alloy.

Turn on the argon supplies and set the flow-rates to the upper and lower inlets at about 1 $dm^3\ min^{-1}$ and 100 $cm^3\ min^{-1}$, respectively, with the top valve closed. Turn on the induction generator according to the manufacturer's instructions and bring the graphite core up to the required temperature (see Table I) over a period of about 20 min. Allow the temperature to stabilise for a further 10 min. The temperature of the furnace is determined by opening both valves and looking down through the optical pyrometer and the open valves into the base of the furnace. Close the top valve.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE DETERMINATION OF BISMUTH

Concentration range/$\mu g\ g^{-1}$	Wavelength/nm	Mass range of sample/mg	Temperature of graphite core/°C
15–200	227.6	2–10	1650–1750
1–30	306.8	2–12	1800–2000
<3	306.8	1–12	2050–2200

Pull out the shutters, select the appropriate wavelength on the atomic-absorption spectrophotometer (see Table I) and push in the shutters. This procedure is carried out only once, at the beginning of a run. Open the top valve, close the bottom valve and drop a sample into the space between the valves. Close tap T_1, wait until the reading on the flow meter reaches zero, then close tap T_2 and immediately close the top valve. Pull out the shutters and press the auto zero button to set to zero absorbance. Switch on the recorder. Open the bottom valve to allow the sample to drop on to the base of the graphite core. The alloy melts and a cloud of atomic vapour, including the bismuth in the sample, is released into the light path, thus producing an absorbance peak on the recorder. When the recorder pen has fallen to about 10% of the peak absorbance, typically in 10–20 s, switch off the recorder and push in the shutters. Open tap T_2, and then tap T_1, in order to allow argon to purge the cloud of bismuth vapour from the furnace. Allow at least 2 min before adding the next sample. Continue in this manner until all of the samples have been added to the furnace. If peak absorbances are expected to be less than 0.1, use a scale expansion of $\times 5$.

Reduce the power to the furnace from the generator gradually over a period of 15 min. Switch off the induction generator but continue to pass argon down the graphite core and water through the cooling panels until the core has reached room temperature.

Calibration Graphs

For the determination of bismuth in steels, calibration graphs of peak absorbance *versus* amount of bismuth are obtained by dropping increasing amounts of BCS 330, which can be taken to contain 3.0 $\mu g\ g^{-1}$ of bismuth, into the graphite core under conditions capable of

producing absorbances up to 1.0. For the determination of bismuth in cast irons, calibration graphs are obtained by dropping into the graphite core suitable amounts of stainless steels SS2, SS3 and SS4, containing 50, 68 and 105 $\mu g\ g^{-1}$ of bismuth, respectively. These alloys have been analysed to determine their bismuth contents in a collaborative study.[13] The amounts of alloys are selected to produce absorbances up to 1.0.

Calibration graphs can also be obtained for 1–25 and 25–300 ng of bismuth from aqueous solution using wavelengths of 306.8 and 227.7 nm, respectively, and core temperatures of approximately 2100 and 1700 °C, respectively. Suitable volumes of standard bismuth nitrate solution A or B are dispensed on to carbon discs (3 mm thick × 6.5 mm diameter) cut from Specpure carbon rod, these discs having been previously baked at 600 °C in an atmosphere of argon. The discs are dried under an infrared lamp for 30 s and then dropped into the graphite core. When the furnace is cool the used pellets are removed from the furnace well.

Analysis of Steels or Cast Irons for Bismuth

When a series of steels is being analysed suitable amounts are dropped into the graphite core over a period of 2–3 h and, during the same run, a variety of masses of BCS 330 are also added for the purpose of constructing a calibration graph, generally at the beginning of the run. At the end of the run the calibration graph is drawn and the mass of bismuth in each sample of steel is obtained from the graph. The concentrations of bismuth in the steels are then calculated. This is the best procedure to adopt because the absorbance peak for a particular mass of bismuth is temperature dependent and it is not worthwhile wasting time in bringing the temperature of the core to exactly the same value from one run to the next.

If cast irons are to be analysed, a similar procedure should be adopted.

Results

Typical calibration graphs prepared from BCS 330, from stainless steel SS2 and from bismuth nitrate solutions are shown in Figs. 3 and 4. The calibration graphs for the solutions had gradients that were about 10% different from those for the steels.

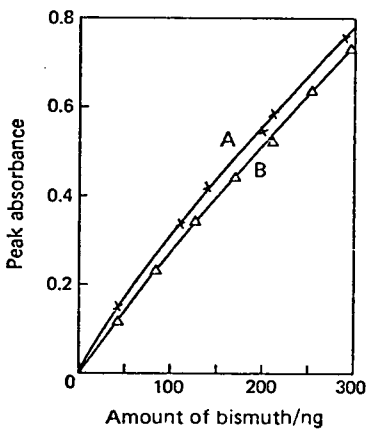

Fig. 3. Calibration graphs for bismuth in cast irons obtained with A, varying masses of stainless steel SS2, and B, varying volumes of bismuth nitrate solution A. Temperature of core, 1730 °C; resonance line, 227.7 nm.

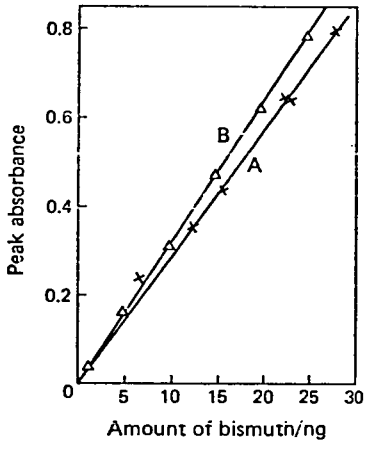

Fig. 4. Calibration graphs for bismuth in steels obtained with A, varying masses of mild steel BCS 330, and B, varying volumes of bismuth nitrate solution B. Temperature of core, 2070 °C; resonance line, 306.8 nm.

Many steels have been analysed to determine their bismuth content by dropping 1–12-mg samples into the furnace, usually at a temperature of 2100 °C. The results are shown in Table II, the reported bismuth content being the average of at least two determinations.

TABLE II

RESULTS FOR THE DETERMINATION OF BISMUTH IN STEELS

Steel	Average result/μg g^{-1}	Steel	Average result/μg g^{-1}
BCS 218/3	0.02	BCS 336	3.4
239/3	0.08	337	0.036
260/3	<0.004	338	0.052
277	0.07	339	0.05
320	0.55	340	0.04
321	0.071	341	0.05
322	0.074	342	0.6
323	0.057	451	0.20
324	0.071	452	0.093
325	0.35	453	0.087
326	0.031	454	0.10
327	0.038	455	0.086
328	0.055	456	0.014
329	26	457	0.012
330	3.0*	458	0.022
331	0.055	459	0.012
332	0.088	460	0.016
333	0.060	SS1 (Type 310)	0.010
334	0.047	JK† 1C	0.006
335	0.062	2C	0.010

*Assumed value.
†JK 1C is an ultra-pure mild steel; JK 2C is a low-alloy steel.

The limit of detection of the method is 0.004 μg g^{-1}. The limit was determined by dropping 11 samples of BCS 327, approximately 10 mg in mass, into the furnace and obtaining the standard deviations of the peak heights normalised to exactly 10 mg of each sample. The limit of detection is twice the standard deviation (0.002 μg g^{-1}).

Results for the determination of bismuth in nine cast irons are shown in Table III.

TABLE III

RESULTS FOR THE DETERMINATION OF BISMUTH IN CAST IRONS OBTAINED BY VARIOUS WORKERS

	Bismuth content/μg g^{-1}				
			Hunter *et al.*[9]		
Cast iron	BCIRA	Headridge and Richardson[14]	C furnace	C filament	Described method
D1	85	82			75
2	130	131			121
3	16	15	16	26	18
4	65	62	90	84	68
5	180	184			187
6	85	84			86
7	19	21			28
8	63	60	65	71	69
9	90	92	88	105	97

The precision of the method has been determined on numerous occasions and typical results are shown in Table IV.

TABLE IV

PRECISIONS OBTAINED WITH THE INDUCTION FURNACE METHOD

Alloy	Number of determinations	Relative standard deviation, %
BCS 327	11	5.6
BCS 330	6	2.9, 7.2, 7.7, 9.9
BCS 336	6	3.4, 8.4
Cast iron D8	6	3.0

Discussion

The results for stainless steels SS2, SS3 and SS4 were obtained as a result of a collaborative study and are likely to be fairly accurate.[13] However, SS2 contains the lowest concentration of bismuth, at 50 $\mu g\ g^{-1}$, and this is not a suitable standard for steels containing less than 5 $\mu g\ g^{-1}$ of bismuth. A search of the literature revealed that BCS 330 had been analysed to determine bismuth by Frech,[7] Fleming and Ide[8] and Hunter *et al.*,[9] who reported the concentration of bismuth to be 2.8, 3 and 3.4 $\mu g\ g^{-1}$, respectively. Therefore, in this investigation, the concentration of bismuth in BCS 330, used as the standard for steels, was taken to be 3.0 $\mu g\ g^{-1}$. However, in the absence of a solid standard it should still be possible to obtain semi-quantitative results for the determination of bismuth in steels and cast irons by using standard bismuth nitrate solutions. It can be seen from Figs. 3 and 4 that the calibration graphs for solid samples and solutions are not coincident but their slopes do not differ appreciably. Because of the different sequence of events in the production of bismuth atoms from metal samples and bismuth nitrate deposits on graphite discs it is not surprising that the calibration graphs are not coincident. In fact, only a few calibration graphs have been obtained from solutions and it would be of considerable interest to compare calibration graphs obtained from standard steels and standard bismuth nitrate solutions over a wide range of temperatures.

The shapes of the absorbance peaks at 1660 and at 2200 °C are shown in Fig. 5 for two steels. As the temperature increases the width of the peak decreases. Absorbance peaks for bismuth nitrate on graphite discs at 1730 °C were slightly broader than peaks of identical height for bismuth from steel at the same temperature. Absorbance peaks of the same height for bismuth nitrate on graphite discs and for bismuth from steel were the same shape at 2070 °C. The width at half the absorbance peak height, expressed in seconds, is greater than that usually obtained with a Massmann furnace. This is because the volume of the graphite core and side-arms is greater than the volume of a Massmann furnace and the flow-rate of stir gas is fairly low at 100 $cm^{-3}\ min^{-1}$.

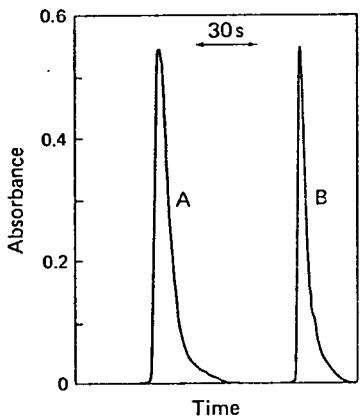

Fig. 5. Absorbance peaks for A, 181 ng of bismuth from steel SS2 at 1660 °C using the line at 227.7 nm, and B, 21.8 ng of bismuth from steel BCS 330 at 2200 °C using the line at 306.8 nm.

Information on the accuracy of the results given in Tables II and III can be obtained by comparing these results with those obtained by use of other methods. This is done in Tables III and V. Satisfactory agreement between our results and those of other workers has been obtained in most instances, and the results for BCS 329 and 336 are particularly informative. Normally, calibration at the beginning of a run is adequate for up to 3 h. If the very best accuracy that can be achieved with the furnace has to be guaranteed, then two samples of the standard alloy can be added after every ten samples to verify that no drift associated with changes in temperature or the argon flow-rate has occurred. In practice, the tem-

perature of the core and the flow-rate of argon have been found to be steady during a run.

In Table II the results for BCS 218/3, 239/3, 277, 339, 340, 341 and 342 are reported to only one significant figure because the graphite core was nearing the end of its useful life when these determinations were made. Increased scatter in the results and poorer sensitivities are found when the time for replacing a core is near.

TABLE V

RESULTS FOR THE DETERMINATION OF BISMUTH IN STEELS OBTAINED BY VARIOUS WORKERS

Steel	Bismuth content/μg g^{-1}				
	Hunter *et al.*[9]	Fleming and Ide[8]	Frech[7]	Attwell and Golden[5]	Described method
BCS 239/3		<1			0.08
320	0.8	<1			0.55
321	<0.4	<1			0.071
322		<1			0.074
323		<1			0.057
324		<1			0.071
325	0.4	<1			0.35
326	<0.4	<1			0.031
327		<1			0.038
328		<1			0.055
329	23, 34*	22			26
330	3.4	3	2.8		3.0†
334				<0.2	0.047
335				<0.2	0.062
336			3.2	4.0	3.4
337				<0.2	0.036
JK 1C			<0.5		0.006
2C			<0.5		0.010
Limit of detection	0.4	1	0.5	0.2	0.004

* Using a carbon filament, otherwise with a carbon furnace.
† Assumed value.

Leaving these seven results out of consideration, most of the other bismuth contents reported in Table II should be within 10% of the actual values provided that the bismuth content is in excess of 0.04 μg g^{-1} and assuming that the bismuth content of BCS 330 is exactly 3.0 μg g^{-1}. The accuracy will be poorer at concentrations less than 0.04 μg g^{-1}. These statements are made on the assumption that other elements in the steels that have appreciable vapour pressures at 2 100 °C are without effect on the bismuth peak heights.

It is likely that manganese (0.45% in the standard, BCS 330) would be the element producing most atoms in the light path at 2100 °C; manganese boils at 2150 °C. For BCS 329 and 336, the method described in this paper has produced bismuth contents of 26 and 3.4 μg g^{-1}, respectively, which are in good agreement with the results of other workers, namely 23 and 22 μg g^{-1} and 3.2 and 4.0 μg g^{-1}, respectively. However, BCS 329 and BCS 336 contain 0.12 and 0.81% of manganese, respectively, which are different values from the 0.45% in BCS 330. Also, when 0.5- and 1.7-mg samples of Specpure manganese were dropped into the furnace (five times to several hundred times more manganese than in the steel samples) no detectable absorbance readings resulted, indicating that there is no scattering of light from atoms in the light path. In addition, a calibration graph was prepared at 2 250 °C using 4.7–9.4-mg samples of BCS 330 and, in the same run, 4.7 mg of BCS 330 plus 6.0 mg of Specpure manganese, and 9.7 mg of BCS 330 plus 4.0 mg of Specpure manganese, were added to the furnace. The two peak absorbances also lay on the calibration graph. Therefore, it appears that various amounts of manganese in steels and of other more volatile elements that produce atoms in the light path at much lower concentrations probably have little effect on the accuracy of the results.

Most steels contain low concentrations of sulphur, phosphorus, arsenic and antimony. If part or all of these elements is released into the gas phase when alloy samples are dropped

into the graphite core, then these elements may be present as molecules in the light path and the possibility of molecular absorption at the wavelength of the bismuth resonance lines cannot be overlooked. To test for possible molecular absorption the bismuth hollow-cathode lamp was replaced with a deuterium lamp and samples of a steel known to contain sulphur, phosphorus, arsenic and antimony were dropped into the furnace with instrumental settings of 306.8 nm and slit width 0.2 nm. In all instances the absorbance was zero, showing that molecular absorption was absent.

For the cast irons, fairly good agreement has been obtained between our results and those of others when it is considered that the only suitable metal standards available for the cast irons were the series of three stainless steels with compositions appreciably different from those of cast irons.

The precisions shown in Table IV are typical of those obtained with the induction furnace. The variations in relative standard deviation are due mainly to some inhomogeneity in the samples, and the effect of taking only six samples. For a perfectly homogeneous material the relative standard deviations are expected to be about 2–4%. Poorer precision is found as the core nears the end of its useful life, as was mentioned above. This phenomenon may be associated with a more turbulent flow of argon through a furnace core that has suffered erosion during use. If the relative standard deviation for an alloy exceeds 10%, it is advisable first to check the equipment with an alloy such as BCS 330 in order to make sure that the graphite core is vertical and properly aligned with the light beam and graphite funnel and that no deterioration in the performance of the atomic-absorption spectrophotometer has occurred. If a good precision is still obtained for BCS 330, then one can suspect that the relative standard deviation in excess of 10% for the other alloy under investigation is caused by appreciable inhomogeneity in the sample with respect to bismuth. Certainly a criticism of this very sensitive method for determining bismuth in metals is that the small samples may not be representative of the material as a whole. This is a particularly valid criticism if inhomogeneity of the material under study is to be expected. However, it is easy to test for inhomogeneity by adding, say, six samples of the material to the furnace and obtaining the relative standard deviation for the concentration of bismuth. For the steels and cast irons investigated by the author no evidence of excessive scatter due to segregation was found in the results.

The limit of detection at 0.004 $\mu g\ g^{-1}$ is 50 times better than the previous best for steels.[5] If necessary, it should be possible to improve it even further by using the most sensitive resonance line for bismuth at 223.1 nm. However, the intensity of this line from the Pye Unicam hollow-cathode lamp was rather low and, therefore, the 223.1-nm line was not used by us.

Samples can be dropped into the furnace at 2-min intervals, although it is advisable to extend the time interval between the additions of samples to 5 min if results of the highest precision are required. This increased interval is to ensure that all of the bismuth from one sample is completely removed from the furnace, particularly from the side-arms, before the next sample is added. Usually a hot core lasts for at least 50 h and no problems have been experienced with build-up of material in the bottom of the well. A core, at present being employed for the determination of lead in steels, has been in operation for approximately 45 h, is still producing satisfactory results and has had added to it 475 samples, *i.e.*, about 2.4 g of steel. In the early studies with this furnace, the annular graphite rings on the ends of the side-arms were not fitted and the life of the core was very dependent on the rate at which the graphite ends of the side-arms eroded, being finally terminated when the graphite powder insulation spilled out of the side-arms. This erosion occurred in spite of the removal of traces of oxygen from the argon gas. It may have been caused by oxidation of the graphite during the out-gassing of air as the temperature of the furnace was raised at the start of a run. Also, the flow of purge gas through the graphite core may have been insufficient to remove rapidly all of the air from the Sindanyo box, thus producing slow erosion effects on the outside of the graphite. Placing the annular graphite rings on the ends of the side-arms has prolonged the life of a graphite core very considerably. The erosion of the graphite now occurs on the periphery of the rings, where it is of little consequence, and the life of the core assembly is usually terminated by a marked deterioration in the condition of the silica sheath.

At present the furnace is being employed to investigate the determination of a wide range of troublesome elements in steels and nickel-base and copper-base alloys.

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DETERMINATION OF SILVER IN IRONS AND STEELS BY ATOMIC-ABSORPTION SPECTROMETRY WITH AN INDUCTION FURNACE: DIRECT ANALYSIS OF SOLID SAMPLES

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Summary—The silver contents of 17 irons and steels have been determined by dropping 0.5–20 mg of millings or turnings of the metals into an induction furnace situated within an atomic-absorption spectrophotometer. The limit of detection was 0.005 μg/g and the relative standard deviations were 12% or better for silver contents of not less than 0.05 μg/g. Samples are added to the furnace at 4–5 min intervals.

Metals or metalloids of low melting-point such as thallium, tin, lead, arsenic, antimony, bismuth, selenium, tellurium and silver are known to have detrimental effects on the properties of certain steels and of nickel-base alloys when present in very low concentrations, often less than 10 μg/g. Of these, silver is stated to impair the hot workability of stainless steels when present at trace levels[1] and, according to a General Electric Co. specification covering wrought and cast nickel-cobalt-base alloys,[2] the concentration of silver should not exceed 5 μg/g. Actually steels seldom contain silver in concentrations in excess of 1 μg/g unless the element has been deliberately added.

Golden and Atwell[3] have determined silver in ingot irons by d.c. arc emission spectrography after preconcentration of silver as sulphide, with molybdenum as a carrier. With a triple exposure the limit of detection for iron samples was reported to be 0.2 μg/g. Hofton[4] has determined silver in steels by atomic-absorption spectrometry after a straightforward dissolution procedure. The calculated detection limit was 1.1 μg/g but Hofton quoted results only for the determination of silver in prepared steels containing 90–200 μg of silver per g. Burke[5] has determined silver in aluminium-, iron- and nickel-base alloys by atomic-absorption spectrometry after extraction as an ion-association complex from hydrochloric acid solution containing ascorbic acid and potassium iodide, into a solution of trioctylphosphine oxide in 4-methylpentan-2-one, with a limit of detection of 0.05 μg/g. Dulski and Bixler[6] have applied the method of Burke[5] and a method based on dissolution in nitric acid followed by atomic-absorption spectrometry with a heated graphite atomizer for the determination of silver in four irons and steels. With the heated graphite atomizer, the limit of detection was ≤0.02 μg/g of silver.

However, spectrographic methods following preconcentration, and methods involving dissolution followed by atomic-absorption spectrometry, are relatively slow and, therefore, we have applied atomic-absorption spectroscopy with an induction furnace to the direct determination of silver in solid samples of irons and steels. The method is similar to that already described for the determination of trace levels of bismuth in steels and cast irons.[7]

EXPERIMENTAL

Materials and reagents

Standard irons and steels. British Chemical Standards, National Bureau of Standards alloys, and alloys from the Institutet för Metallforskning, Sweden.

Silver nitrate, Engelhard photographic quality.

Standard silver nitrate solution A (500 μg/ml silver concentration). Dissolve 0.787 g of silver nitrate in 50 ml of distilled water and dilute to 1 litre with 0.16*M* nitric acid.

Standard silver nitrate solution B (silver 0.1 μg/ml). Prepare freshly each day by a series of appropriate dilutions of solution A with 0.16*M* nitric acid.

Apparatus and method for obtaining absorbances for a series of solid samples

These were identical to those previously described[7] except that the graphite core and side-arms were made from AGTS grade graphite (British Acheson Electrodes), which had been previously baked for about 10 hr under vacuum at 2200°. The resonance line at 328.1 nm from a silver hollow-cathode lamp (Activion Glass Ltd.) was used with a band-width of 0.2 nm on the Perkin Elmer 300 S atomic-absorption spectrophotometer. The experimental conditions for the determination of silver are shown in Table 1. The temperature of the furnace core should be approximately 2270°.

Table 1. Experimental conditions for the determination of silver

Concentration range μg/g	Mass range of sample, mg	Damping position	Scale expansion
0.2–5	0.5–10	4	None
0.05–1	2–10	1	None
<0.05	5–20	1	×5

Calibration graphs

For the determination of silver in steels containing 0.2–5 μg/g, calibration graphs of peak absorbance *vs.* amount of silver are obtained by dropping increasing amounts of NBS standard steel SRM 361, which can be taken to have a silver content of 4.0 μg/g, into the graphite core under conditions capable of producing absorbances up to 1.0. The silver contents of steels containing <1 μg/g may be determined by employing the standardized steel JK 2C in a similar way to obtain the calibration graph.

Calibration graphs can also be obtained for 0.5–3 ng of silver in aqueous solution by using a core temperature of approximately 2270°. Suitable volumes of standard silver nitrate solution B are dispensed from glass microlitre pipettes onto carbon discs (3 mm thick × 6.5 mm diameter) cut from "Specpure" carbon rod, these discs having been previously baked under vacuum at 2200°. The discs are dried under an infrared lamp for 30 sec and then dropped into the graphite core.

Analysis of irons and steels for silver

When a series of irons and steels is being analysed, suitable amounts are dropped into the graphite core over a period of 2–3 hr and, during the same run, various masses of SRM 361 or JK 2C are also added for the purpose of constructing a calibration graph, generally at the beginning of the run. When the run is completed, the calibration graph is drawn and the mass of silver in each sample is obtained from the graph. The concentrations of silver in the samples are then calculated.

RESULTS AND DISCUSSION

The method of direct analysis of solid samples is very sensitive and calibration graphs must be constructed with damped absorbances for standards containing more than 1 μg of silver per g, if the apparent absorbances towards the upper end of the calibration graph are to be less than 1.0. Because of the damping, the calibration graph is then a curve, as it is when constructed from different masses of SRM 361 corresponding to 2–10 ng of silver. However, calibration graphs for 0.2–3 ng of silver, constructed with JK 2C (silver 0.36 μg/g) without damping, are straight lines through the origin, the amount of silver giving 1% absorption being approximately 18 pg. A calibration graph for 0.5–3 ng of silver produced from a standard aqueous silver nitrate solution was also a straight line through the origin. The nitric acid used (0.16*M*) containing no added silver nitrate, was shown to contain 7.5 ng of silver per ml by addition of 10 μl to a carbon disc, drying the disc and dropping it into the furnace at 2300°. The calibration graph for silver from solutions was corrected for the silver in the nitric acid.

A series of irons and steels was analysed for silver contents by dropping 2–20 mg samples (degreased with a suitable solvent, dried, weighed to the nearest 10 μg, and transferred with forceps) into the furnace at approximately 2270°. The results are shown in Table 2.

The standard deviations for materials SRM 365, BCS 260/3, 260/4 and 456, and JK 1C are 0.002–0.003 μg/g and hence the limit of detection of the method is 0.005 μg/g.

Before it was decided to standardize JK 2C for the calibration graphs for the analysis of irons and steels containing <0.2 μg of silver per g, a few materials containing 0.1–0.2 μg of silver per g were analysed with use of a calibration graph constructed with SRM 361. The silver contents found for SRM 364 and BCS 451, 452 and 453 were 0.10, 0.10, 0.19 and 0.13 μg/g respectively with relative standard deviations (eight replicates) of 5, 9, 9 and 9% respectively.

SRM 1261 (which is SRM 361 in rod form) is certified to contain 4 μg of silver per g and thus SRM 361 is a suitable standard and can be assumed to have the same silver content as SRM 1261. The silver content of SRM 361 or 1261 has been determined as 3.6 and 4.0 μg/g by Paulsen *et al.*,[8] 4 μg/g by Burke,[5] 3.4 μg/g by Kirk *et al.*,[9] and 4.4 and 4.6 μg/g by Dulski *et al.*[6] An average value of 4.0 μg/g was chosen for the silver content of SRM 361.

The precision of our method is considered to be satisfactory. The most commonly occurring element existing at appreciable concentrations in steels and volatile at 2270° is manganese (b.p. 2150°). For certain steels a relatively high concentration of manganese atoms would be produced in the light-path of the furnace. To check that no light in the region of the 328.1 nm line from the silver hollow-cathode lamp would be scattered by manganese atoms, 4.6–7.1-mg samples of "Specpure" manganese were dropped into the furnace while light of wavelengths 323.2,

Table 2. Results for the determination of silver in irons and steels

Iron or steel	Type	No. of samples analysed	Average result, μg/g	Relative standard deviation, %
SRM 361	AISI 4340 steel	—	4.0*	—
364	High-C steel (modified)	6	0.13	7
365	Electrolytic iron	10	0.015	17
BCS 149/3	High purity iron	5	0.039	27
260/3	"	9	0.006	45
260/4	"	14	0.005	38
451	Mild steel	5	0.10	7
452	"	6	0.19	12
453	"	5	0.15	5
454	"	6	0.12	6
455	"	6	0.11	4
456	"	5	0.020	12
457	"	6	0.18	10
458	"	6	0.31	6
459	"	6	0.10	6
460	"	6	0.052	10
JK 1C	Iron	5	0.014	14
2C	0.2%C steel	12	0.36	5

* Assumed to be same as certified value for SRM 1261 (the rod form of this standard).

Table 3. Results for the determination of silver in irons and steels containing < 1 μg/g.

Iron or steel	Certificate value* μg/g	Results reported by		
		Burke[5] μg/g	Dulski *et al.*,[6] μg/g	This study, μg/g
SRM 364	0.5 and 0.2†			0.13
365	~0.02‡	0.08	0.02	0.015
BCS 149/3		0.05		0.030
260/3		< 0.05		0.006
JK 1C	< 0.1			0.014

* Single determination.
† SRM 1264.
‡ SRM 1265.

323.9, 326.7, 331.7, 332.2 and 334.4 nm successively, from non-resonance antimony lines, passed through the furnace. In no case was any absorbance recorded. To test for possible molecular absorption from any volatile non-metallic elements that might be released from steels at 2270°, the silver hollow-cathode lamp was replaced with a deuterium lamp, and six samples of steel JK 2C (known to contain sulphur, phosphorus, arsenic and antimony) were dropped into the furnace with instrumental settings of 328.1 nm and band-width 0.2 nm. In all cases the absorbances were zero, showing that there was no molecular absorption.

These observations lead us to believe that the silver contents reported in Table 2 are of good accuracy. Our confidence is reinforced by the fact that the furnace has also been used in a similar way to determine the lead contents of sixteen irons and steels, which are standards for lead, with good agreement between the concentrations of lead as determined by us and as reported on the certificates.[10] Unfortunately there are no irons or steels with silver contents less than 1 μg/g that are standards for that element. The silver contents of a few of the alloys used in this study have been reported by other investigators and a comparison of our results with theirs is shown in Table 3.

As far as it is possible to make a comparison, our results are in reasonable agreement with those of others. The results for SRM 364 and BCS 451, 452 and 453 obtained by using a calibration graph prepared from SRM 361 are less accurate than those shown in Table 2 because the small peak absorbances are outside the recommended range for more accurate results. However the agreement between both sets of results is still quite good.

The method is fairly fast, with weighed turnings or millings of an iron or steel being added to the furnace at intervals of 4–5 min. Calibration graphs for silver obtained from steel JK 2C and from aqueous solution, produced from absorbances obtained in the same run at 2260°, were not identical, the absorbance peak being 16% larger for the same amount of silver obtained from solution than from the steel (possibly release of silver from the globule of molten steel is slower than that from silver nitrate). However in the absence of a suitable steel standard for silver, it should be possible to obtain semiquantitative results by constructing a calibration graph by use of suitable volumes of standard silver nitrate solution.

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Determination of Lead in Irons and Steels by Atomic-absorption Spectrophotometry with the Introduction of Solid Samples into an Induction Furnace

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Atomic-absorption spectrophotometry with an induction furnace has been used for the determination of 0.1–100 $\mu g\ g^{-1}$ of lead in 1–12-mg samples of irons and steels dropped into the furnace. Calibration graphs of peak absorbance *versus* mass of lead have been constructed by using standard steels.

Samples of alloys can be added to the furnace at 4–5-min intervals. Information is presented on the calibration graphs and on the accuracy, precision and limits of detection of the method for 44 irons and steels. With steels containing more than 1 $\mu g\ g^{-1}$ of lead relative standard deviations are usually $\leqslant 10\%$. The limit of detection for lead is $\leqslant 0.05\ \mu g\ g^{-1}$ when using this method.

Keywords: *Lead determination*; *iron analysis*; *steel analysis*; *atomic-absorption spectrophotometry*; *induction furnace*

The presence of low concentrations of lead can cause problems with austenitic stainless steels. Edge cracking in ingots of 18Cr-8Ni steel results from the presence of 50 $\mu g\ g^{-1}$ of lead[1] and to prevent hot cracking during forging and rolling of stainless steels a maximum lead content of 30 $\mu g\ g^{-1}$ has been stipulated.[2] Also, a reduction in notched tensile strength is produced by 50 $\mu g\ g^{-1}$ of lead in maraging steels.[3] The presence of lead impairs the formation of spheroidal graphite in cast iron treated with magnesium and a maximum content of 20 $\mu g\ g^{-1}$ has been suggested.[4] Therefore, there is a need for methods of determination of lead in irons and steels at concentrations of less than 100 $\mu g\ g^{-1}$ and many papers have been published on this subject. Information on methods for the determination of lead in steels is presented in Table I.

TABLE I

METHODS FOR THE DETERMINATION OF LEAD IN STEELS

Method	Concentration range for lead/$\mu g\ g^{-1}$	Reference
D.c. arc emission after pre-concentration by precipitation of PbS in CuS	0.5–50	5
D.c. arc emission using Li_2CO_3 flux	0.4–30	6
Absorption spectrophotometry of Pb - dithizone complex after solvent extraction	5–500	7
Differential cathode-ray polarography after solvent extraction	~0.2–500	8
Anodic stripping voltammetry	1–150	9
Flame atomic-absorption spectrophotometry of Pb(II) in 4-methylpentan-2-one after solvent extraction	10–100	10
Atomic-absorption spectrophotometry after hydride generation	7–2300	11
Atomic-absorption spectrophotometry with carbon furnace atomisation after dissolution of the alloy	0.5–150	12
	0.3–100	13
	~0.5–160	14
	0.1–280	15

The methods involving a pre-concentration step are lengthy and, for very low levels of lead, the risk of contamination through lead pick-up increases as the method becomes more involved. Undoubtedly the most convenient method to date appears to be atomic-absorption spectrophotometry with carbon furnace atomisation after dissolution of the alloy in acidic solution. However, at very low trace levels problems can still arise from minute concentrations of lead in acid and in the plastic tips of micropipettes.[15] These problems are eliminated when a direct analysis is carried out on solid samples. Andrews and Headridge[16] have determined bismuth in steels and cast irons by means of atomic-absorption spectrophotometry with the introduction of solid samples into an induction furnace. A similar procedure is now described for the determination of 0.1–100 $\mu g\ g^{-1}$ of lead in 44 irons and steels. However, whereas standard alloys for bismuth were not available, many alloys standardised for lead content were used in this study and a proper assessment of the accuracy of the induction-furnace method was possible and is reported together with detailed information on precision.

Experimental

Reagents and Materials

Standard irons and steels. British Chemical Standards, alloys from National Bureau of Standards, USA, alloys from the Institutet för Metallforskning, Sweden, and cast irons from the British Cast Iron Research Association.

Samples for analysis. These should preferably be millings or turnings of irons or steels so that no more than three pieces need to be added to the furnace core at the same time. Powdery millings are less suitable, for invariably such samples lead to greater scatter in the results.

Lead nitrate. Analytical-reagent grade, dried overnight under vacuum at room temperature.

Nitric acid (sp. gr. 1.42). Analytical-reagent grade.

Standard lead nitrate solution A (1 000 $\mu g\ ml^{-1}$ of lead). Dissolve 1.599 g of lead nitrate in 100 ml of 1% *V/V* nitric acid and dilute to 1 l with 1% *V/V* nitric acid.

Standard lead nitrate solution B (100 $\mu g\ ml^{-1}$ of lead). Dilute 10 ml of lead nitrate solution A to 100 ml with 1% *V/V* nitric acid.

Apparatus and Method for Determining Absorbances for a Series of Solid Samples

The apparatus and the method were identical with those previously described[16] except that towards the end of the investigation the graphite core and side-arms were made from Ultra "F" Purity Graphite, type UF-4S (Ultra Carbon, USA). Graphite cores and side-arms were usually baked for 1 h under vacuum at about 1300 °C before use. The resonance lines at 261.4 and 283.3 nm from a lead hollow-cathode lamp (Activion Glass Ltd.) were used with a slit width of 0.2 nm on a Perkin-Elmer 300S atomic-absorption spectrophotometer. The experimental conditions for the determination of lead are shown in Table II.

TABLE II

EXPERIMENTAL CONDITIONS FOR THE DETERMINATION OF LEAD

Concentration range/$\mu g\ g^{-1}$	Mass range of sample/mg	Core temperature/ °C	Wavelength/ nm	Damping position*
20–100	2–12	2 000–2 100	261.4	1
1–20	1–12	1 820–2 020	283.3	4
<1	4–12	1 950–2 050	283.3	1

* Damping positions 1 and 4 are for time constants of 0.2 and 10 s, respectively.

Calibration Graphs

For the determination of lead in steels containing 20–100 $\mu g\ g^{-1}$ of lead, calibration graphs of peak absorbance *versus* amount of lead are obtained by dropping increasing amounts of mild steel BCS 327, which contains 105 $\mu g\ g^{-1}$ of lead, into the graphite core under conditions capable of producing absorbances up to 1.0 (see Table II). For irons and steels

containing $<20\ \mu g\ g^{-1}$ of lead, a calibration graph is prepared in a similar way using the standardised steels JK 2C (0.2% of carbon, $4.2\ \mu g\ g^{-1}$ of lead), SRM 362 (low-alloy steel, $4.3\ \mu g\ g^{-1}$ of lead) or BCS 337 (austenitic stainless steel, $12\ \mu g\ g^{-1}$ of lead). BCS 337 is less suitable than JK 2C or SRM 362 for a calibration graph when the concentration of lead in the sample to be analysed is expected to be less than $1\ \mu g\ g^{-1}$.

Calibration graphs can also be obtained for the range 0–2 μg of lead using aqueous solutions, core temperatures of from 1750 to 2150 °C and the lead line at 261.4 nm. Suitable volumes of standard lead nitrate solution B are dispensed from a 10-μl syringe on to carbon discs (3 mm thick × 6.5 mm diameter) cut from Specpure carbon rod, these discs having been previously baked under vacuum at 1400 °C. The discs are dried under an infrared lamp for 30 s and then dropped into the graphite core.

Determination of Lead in Irons and Steels

When a series of irons and steels is to be analysed, suitable masses are dropped into the graphite core over a period of 2–3 h and, during the same run, various masses of BCS 327, BCS 337, JK 2C or SRM 362 are also added, generally at the beginning of the run, for the purpose of constructing a calibration graph. During a run the temperature of the core should not alter by more than ±10 °C. When the run is completed the calibration graph is drawn and the mass of lead in each sample is obtained from the graph. The concentrations of lead in the samples are then calculated.

Results

The method of direct analysis of solid samples was so sensitive that the normal resonance line at 283.3 nm could not be used in the construction of a calibration graph for the range 0–2 μg of lead for the determination of concentrations of lead in the range 20–100 $\mu g\ g^{-1}$. The less sensitive line at 261.4 nm was used instead. The resulting calibration graph passed through the origin and was slightly curved at the upper end. A typical calibration graph is shown in Fig. 1.

The resonance line at 283.3 nm was employed with damping position 4 to construct a calibration graph for the range 0–100 ng of lead for the determination of concentrations of lead between 1 and 20 $\mu g\ g^{-1}$. Because of the damping the calibration graph was a curve that passed through the origin. Such a graph is shown in Fig. 2. Calibration graphs constructed for the range 0–25 ng of lead, with no damping and using the 283.3-nm line, in

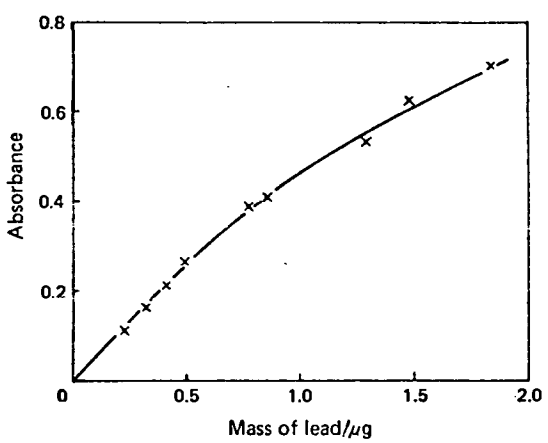

Fig. 1. Calibration graph for the range 20–100 $\mu g\ g^{-1}$ of lead in steels prepared from BCS 327 using the 261.4-nm line and a core temperature of 2050 °C.

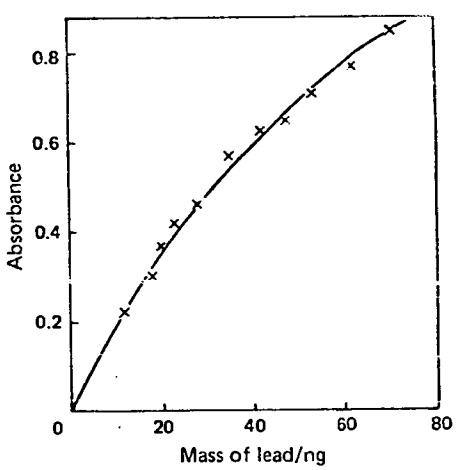

Fig. 2. Calibration graph for the range 1–20 $\mu g\ g^{-1}$ of lead in steels prepared from JK 2C using the 283.3-nm line and a core temperature of 1970 °C.

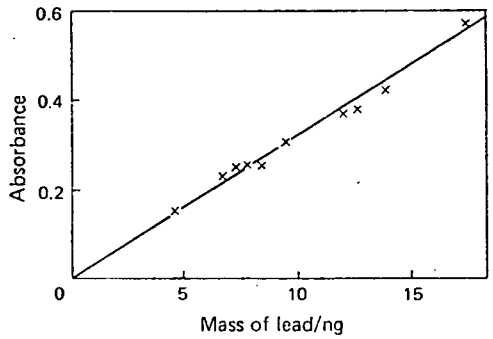

Fig. 3. Calibration graph for concentrations of <1 $\mu g\ g^{-1}$ of lead in steels prepared from SRM 362 using the 283.3-nm line and a core temperature of 1950 °C.

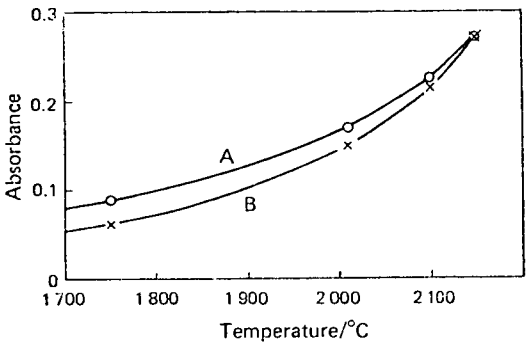

Fig. 4. Peak absorbances at various temperatures for 1 μg of lead from A, lead nitrate solution, and B, mild steel BCS 327.

order to determine concentrations of lead of <1 $\mu g\ g^{-1}$ were straight lines passing through the origin. A calibration graph for this range is shown in Fig. 3.

Calibration graphs prepared for the range 0–2 μg of lead from both BCS 327 and lead nitrate solution B at temperatures in the range 1750–2150 °C were informative. For the solutions they were straight lines passing through the origin, after correcting for a small lead blank resulting from the Specpure graphite discs. For the steel they were slightly curved for amounts of lead up to 1 μg, curving more towards the mass axis for larger amounts. At temperatures up to 2100 °C the calibration graphs for solutions always lay above those for solids, although they approached the curves for solids more closely as the temperature was increased. Peak absorbances for 1 μg of lead from both BCS 327 and solutions are plotted against temperature in Fig. 4. At temperatures between 2120 and 2150 °C, the calibration graphs of peak absorbance *versus* mass of lead up to 1 μg are coincident or almost so for both solutions and mild steel BCS 327. Calibration graphs obtained at 2100 °C are shown in Fig. 5.

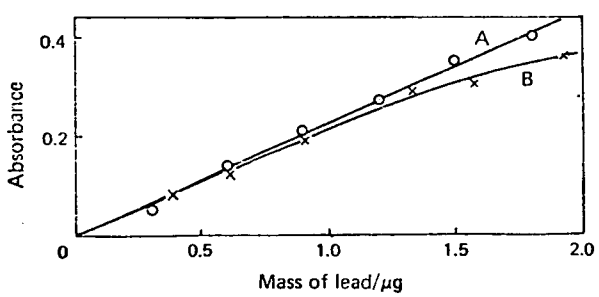

Fig. 5. Calibration graphs for A, 0.3–1.8 μg of lead as lead nitrate and B, 0.3–2.0 μg of lead from BCS 327 using the 261.4-nm line and a core temperature of 2100 °C.

Samples of several series of irons and steels were dropped into the furnace in order to determine their lead contents, using the conditions outlined in Table II. Results are shown in Tables III, IV and V.

The limit of detection of the method was 0.05 $\mu g\ g^{-1}$, calculated as twice the standard deviation obtained for the determination of 15 samples of SRM 365 using SRM 361 for the calibration graph and $\times 5$ scale expansion (see Table V).

Discussion

The results in Table III for the determination of lead in mild steels are in good agreement with the certificate values. The same applies for results in Table IV when a comparison

TABLE III

RESULTS FOR THE DETERMINATION OF LEAD IN MILD STEELS CONTAINING 20–100 $\mu g\ g^{-1}$ OF LEAD

Calibration graph prepared using BCS 327 (105 $\mu g\ g^{-1}$ of lead).

BCS alloy	Lead reported (certificate value)/ $\mu g\ g^{-1}$	Lead found/ $\mu g\ g^{-1}$	Number of samples analysed	Relative standard deviation, %
271	25	23	6	3
272	30*	31	6	5
273	30*	30	6	10
274	85	83	5	5
275	50	56	11	5
276	65*	78	6	7
277	65*	78	6	4
330	30	28	8	5
456	100	98	8	6
457	60	64	7	9
459	30	26	8	11
460	30	24	7	13

*Not fully standardised.

TABLE IV

RESULTS FOR THE DETERMINATION OF LEAD IN IRONS AND STEELS CONTAINING 1–20 $\mu g\ g^{-1}$ OF LEAD

Calibration graphs prepared using JK 2C (4.2 $\mu g\ g^{-1}$) of lead except for results marked.

Alloy	Type	Lead reported (certificate value)/ $\mu g\ g^{-1}$	Lead found/ $\mu g\ g^{-1}$	Number of samples analysed	Relative deviation, %
BCS 320	Mild steel		3.9	6	14
BCS 321	Mild steel		2.6	6	5
BCS 322	Mild steel		1.4	6	6
BCS 323	Mild steel		1.0	5	5
BCS 324	Mild steel		1.2	6	15
BCS 325	Mild steel		2.3	6	6
BCS 331	Austenitic stainless		5.9	5	6
BCS 332	Austenitic stainless		8.2	5	5
BCS 333	Austenitic stainless		6.5	6	2
BCS 334	Austenitic stainless	11	11*	6	5
BCS 335	Austenitic stainless	15	13*	6	8
BCS 336	Austenitic stainless	7	6.9	6	13
BCS 338	Austenitic stainless		5.7	6	3
BCS 339	Ferritic stainless		5.9	6	4
BCS 340	Ferritic stainless		5.6	6	4
BCS 341	Ferritic stainless		7.2	6	2
BCS 342	Ferritic stainless		11	5	3
BCS 451	Mild steel		2.2	6	9
BCS 452	Mild steel		3.8	6	5
BCS 453	Mild steel		5.5	6	5
BCS 454	Mild steel		3.5	6	8
BCS 455	Mild steel		13	6	15
SRM 362	AISI 94B17 steel (modified)	4.3†	3.8	6	10
			4.2	10	6
SRM 363	Cr-V steel (modified)	22‡	19*	5	4
JK 2C	0.2% C steel	4.2§	4.2‖	10	9
D5	Cast iron	4¶	4.1*	6	4
D8	Cast iron	18¶	19*	6	9

* Calibration graph prepared using BCS 337 (12 $\mu g\ g^{-1}$ of lead).
† In the form SRM 1262.[17]
‡ In the form SRM 1263.[17]
§ Not fully standardised.
¶ Value from British Cast Iron Research Association.
‖ Calibration graph prepared using SRM 362 (4.3 $\mu g\ g^{-1}$ of lead).

with certificate values is possible. There is every reason to believe that the other results for lead shown in Table IV are accurate. It will be seen from Tables III and IV that the relative standard deviation of the method at these levels is usually $\leqslant 10\%$. The values of 105 $\mu g\ g^{-1}$ for lead in BCS 327 and of 4.2 $\mu g\ g^{-1}$ for lead in JK 2C are the averages of eleven and three determinations, respectively, reported on the certificates.

TABLE V

RESULTS FOR THE DETERMINATION OF LEAD IN IRONS AND A STEEL CONTAINING $<1\ \mu g\ g^{-1}$ OF LEAD

The numbers in parentheses are the numbers of samples analysed.

Material	Type	Lead content (certificate value)/$\mu g\ g^{-1}$	Lead found*/ $\mu g\ g^{-1}$	Relative standard deviation, %	Lead found†/ $\mu g\ g^{-1}$	Relative standard deviation, %	Lead found‡/ $\mu g\ g^{-1}$	Relative standard deviation, %
SRM 361	AISI 4340 steel	0.25§	0.29	11 (10)	0.25	13 (6)		
SRM 365	Electrolytic iron	0.15‖	0.16	20 (8)	0.13, 0.15	12(6), 19(18)	0.14	19 (15)
JK 1C	Iron	0.5¶	0.26	10 (7)	0.22	15 (6)	0.24	18 (14)
BCS 260/3	High-purity iron		0.38	46 (12)	0.33	47 (6)		
BCS 149/3	High-purity iron		1.0	15 (7)	0.78	18 (6)		

* Calibration graph prepared using SRM 362 (4.3 $\mu g\ g^{-1}$ of lead).
† Calibration graph prepared using JK 2C (4.2 $\mu g\ g^{-1}$ of lead).
‡ Calibration graph prepared using SRM 361 (0.25 $\mu g\ g^{-1}$ of lead).
§ In the form SRM 1261.[17]
‖ In the form SRM 1265.[17]
¶ Single determination.

The results in Table V for the determination of lead in SRM 361 and SRM 365, using both SRM 362 and JK 2C for the calibration graphs, are in good agreement with the certificate values. The values reported in the table for the determination of lead in JK 1C, using the proposed method, are in satisfactory agreement with a value of 0.3 $\mu g\ g^{-1}$ recently reported by Frech.[13] The precision of the method is not as good for levels of lead below 1 $\mu g\ g^{-1}$ as it is for higher levels of lead, but it is still acceptable except for BCS 260/3. The relative standard deviations of 46 and 47% for this iron suggest that the lead is inhomogeneously distributed in the material. The limit of detection of 0.05 $\mu g\ g^{-1}$ reported above is almost certainly too conservative. Absorbances in the region of 0.04 were obtained for the 15 samples of SRM 365 that were analysed in order to calculate the limit of detection. However, no sample of iron could be found that contained less than 0.13 $\mu g\ g^{-1}$ of lead. If a sample had been available to produce absorbances in the region of 0.01, it seems likely that the limit of detection would have been found to be 0.02 $\mu g\ g^{-1}$ of lead or even lower. The amount of lead producing 1% absorption of the 283.3-nm line was approximately 0.17 ng at 2000 °C.

The method is straightforward. Weighed turnings or millings of an iron or steel are added to the furnace at 4–5 min intervals. Most of the work was done with cores and side-arms machined from the same batch of AGW-grade graphite (British Acheson Electrodes), which, after heat treatment in a vacuum, showed no lead background. However, the next batch of AGW-grade graphite produced a high lead background, which could not be removed even after extensive baking under vacuum at 2 200 °C. Therefore it was necessary to finish the work with a core and side-arms made from Ultra "F" Purity Graphite, type UF-4S (Ultra Carbon).

All the results reported in Tables III, IV and V were obtained from calibration graphs prepared by using standardised irons or steels. However, in the absence of a suitable iron or steel standard, it should be possible to construct a calibration graph from standard solutions of lead nitrate at 2120–2150 °C.

We are indebted to the BSC/BISPA Chemical Analysis Committee and the British Steel Corporation for a grant to buy the Perkin-Elmer 300S atomic-absorption spectrophotometer.

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Determination of Antimony and Other Trace Elements in Irons and Steels by Atomic-absorption Spectrophotometry with Introduction of Solid Samples into an Induction Furnace*

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Atomic-absorption spectrophotometry with an induction furnace has been used for the determination of 0.5–350 $\mu g\ g^{-1}$ of antimony in 1–20-mg samples of irons and steels dropped into the furnace. Calibration graphs of peak absorbance *versus* the mass of antimony have been constructed by using standard steels. Information is presented on the accuracy and precision of the method for 13 irons and steels. The limit of detection for antimony is 0.12 $\mu g\ g^{-1}$.

Calibration graphs have also been obtained for indium in a nickel-base alloy and thallium, tin, selenium, tellurium, zinc and cadmium in steels in order to establish the conditions that will be necessary to determine these elements using a procedure similar to that employed for antimony. Factors affecting the volatility of trace elements with boiling-points below 2300 °C are discussed.

Keywords: *Antimony determination*; *trace-element determinations*; *iron and steel analysis*; *atomic-absorption spectrophotometry*; *induction furnace*

The presence of antimony is known to be detrimental to certain mechanical properties of low-alloy steels. As little as 10 $\mu g\ g^{-1}$ produces 350 °C embrittlement and temper brittleness.[1] Low concentrations of antimony also adversely affect the hot workability of stainless steels.[2] There is a continuing need to determine antimony in steels within the range 1–500 $\mu g\ g^{-1}$. Many methods are available for the determination of antimony above 100 $\mu g\ g^{-1}$ but few methods are suitable below this level and only the most sensitive can be employed to determine concentrations of antimony below 10 $\mu g\ g^{-1}$. Information about some of these methods is given in Table I.

TABLE I

METHODS FOR THE DETERMINATION OF ANTIMONY IN STEEL

Method	Concentration range of antimony present/$\mu g\ g^{-1}$	Reference
Molecular-absorption spectrophotometry of rhodamine B complex after solvent extraction	10–500	3
D.c. arc-emission spectrography after pre-concentration by precipitation of Sb_2S_3 on CuS	5–500	4
Hollow-cathode emission spectrometry on solid samples	~0.5–40	5
Flame atomic-absorption spectrophotometry	20–350	6
Flame atomic-absorption spectrophotometry of Sb(III) in 4-methylpentan-2-one after solvent extraction	2–350	7
Flame atomic-absorption spectrophotometry after generation of SbH_3	1–350	8
Atomic-absorption spectrophotometry with carbon-furnace atomisation after dissolution of the alloy	0.7–200 1–350	9 10

Methods involving solvent extraction or other pre-concentration procedures are relatively slow and the most attractive methods so far reported are the atomic-absorption methods involving hydride generation,[8] atomisation in resistively heated carbon furnaces[9,10] and hollow-cathode emission spectrometry.[5] Headridge and co-workers have already reported

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on the determination of bismuth,[11] silver[12] and lead[13] in steels using atomic-absorption spectrophotometry with the introduction of solid samples into an induction furnace. In this paper, results for a similar study on antimony are reported along with data on other volatile elements that might at some time have to be determined in steels containing very low concentrations of these elements.

Experimental

Materials

Standard irons and steels. British Chemical Standards, alloys from the National Bureau of Standards, USA, and alloys from the Institutet för Metallforskning, Sweden.

Samples for analysis. These should preferably be millings or turnings of irons or steels so that no more than three pieces need to be added to the furnace core at the same time.

Apparatus and Method for Determining Absorbances for a Series of Solid Samples

The apparatus and the method were identical with those described previously[11] except that the graphite core and side-arms were made from Ultra Superior Purity Grade graphite (Ultra Carbon) and baked for 6 h under vacuum at about 1900 °C before use. Information on the hollow-cathode lamps used in this work is given in Table II.

TABLE II

DATA ON HOLLOW-CATHODE LAMPS

Element	Manufacturer	Line employed/nm	Lamp current used/mA
Antimony	Pye Unicam	231.1	10
Indium	Pye Unicam	303.9	5
Thallium	Perkin-Elmer	276.8	20
Tin	Activion	286.3	20
Selenium	Activion	196.0	6
Tellurium	EMI	214.3	5
Zinc	Activion	213.9	8
Cadmium	Activion	228.8	13

In all instances, except for selenium, a slit width of 0.2 nm was used on a Perkin-Elmer 300S atomic-absorption spectrophotometer; the slit width used for selenium was 0.7 nm. The experimental conditions for the determination of antimony are shown in Table III.

Calibration Graphs

Antimony

For the determination of antimony in irons and steels containing less than 150 $\mu g\ g^{-1}$ of antimony, calibration graphs of peak absorbance *versus* the amount of antimony are obtained by dropping increasing amounts of 0.2% carbon steel JK2C, which contains 29 $\mu g\ g^{-1}$ of antimony, into the graphite core under conditions capable of producing absorbances of up to 1.0 (see Table III). For steels containing 150–350 $\mu g\ g^{-1}$ of antimony, a calibration graph is prepared in a similar way using mild steel BCS 328 containing 260 $\mu g\ g^{-1}$ of antimony.

Other elements

Although series of irons and steels were not analysed for these elements, the conditions necessary for obtaining a calibration graph for each element in steel were established using one standard alloy in each instance. These conditions are given in Table IV.

TABLE III

EXPERIMENTAL CONDITIONS FOR THE DETERMINATION OF ANTIMONY

Concentration range/$\mu g\ g^{-1}$	Mass range of sample/mg	Core temperature/ °C	Damping*	Scale expansion
<5	10–20	2620	1	×5
5–150	1–10	2550–2640	1	×1
150–350	1–6	1810	4	×1

* Damping positions 1 and 4 are for time constants of 0.2 and 10 s, respectively.

Determination of Antimony in Irons and Steels

Irons and steels with a silicon to antimony ratio >5:1

When a series of irons and steels is to be analysed, suitable masses are dropped into the graphite core over a period of 2–3 h and, during the same run, various masses of JK2C or BCS 328 are also added, generally at the beginning of the run, for the purpose of constructing a calibration graph. During a run the temperature of the core should not alter by more than ±10 °C. When the run is completed the calibration graph is drawn and the mass of antimony in each sample is obtained from the graph. The concentrations of antimony in the samples are then calculated.

Irons and steels with a silicon to antimony ratio <5:1

The procedure is similar to that above except that 5 g of silicon powder (BDH Chemicals Ltd.) are added to the cold core and well tamped down with a glass rod before the core is heated at approximately 1900 °C, as read on the optical pyrometer, for a sufficient period of time to remove all antimony from the silicon (12 h in our case); samples may then be added to the core.

TABLE IV

EXPERIMENTAL CONDITIONS FOR OBTAINING CALIBRATION GRAPHS FOR CERTAIN MORE VOLATILE ELEMENTS IN STEEL

Damping position 1 (time constant 0.2 s) was used in all instances except zinc, for which damping position 5 (time constant 30 s) was employed.

Element	Standard alloy	Content/ $\mu g\ g^{-1}$	Mass range of sample/mg	Core temperature/ °C	Scale expansion
Indium	R3387*	~10	9–15	2370	×1
Thallium	BCS 312	0.3†	1–13	2330	×5
Tin	BCS 323	240	2–20	2450	×1
Selenium	SRM 361	40‡	3–30	2430	×1
Tellurium	SRM 361	6‡	1–7	2350	×1
Zinc	JK1C	2.0	1–7	1570	×1
Cadmium	JK2C	~0.03	8–35	2350	×5

* A nickel-base alloy.
† See reference 14.
‡ Value for SRM 1261.

Results

The calibration graphs for the range 0–360 ng of antimony obtained with steel JK2C passed through the origin and were slightly curved at the upper end. The mass for 1% absorption was 1.4 ng, this value being obtained from a typical calibration graph for antimony at 2630 °C. The calibration graph for the range 0–1.6 μg of antimony obtained with steel BCS 328 also passed through the origin but was appreciably curved because of the damping applied to the amplifier signals. This damping was necessary in order to keep the apparent absorbance readings below 1.0.

Samples of a series of irons and steels were dropped into the furnace in order to obtain their antimony contents using the conditions outlined in Table III and in the section entitled Determination of Antimony in Irons and Steels. The results are shown in Table V.

TABLE V

RESULTS FOR THE DETERMINATION OF ANTIMONY IN IRONS AND STEELS

Calibration graph prepared using JK2C (29 $\mu g\ g^{-1}$ of antimony), except for results marked ‡, when BCS 328 (260 $\mu g\ g^{-1}$ of antimony) was used.

Alloy	Antimony reported/ $\mu g\ g^{-1}$	Antimony found/$\mu g\ g^{-1}$	Number of samples analysed	Relative standard deviation, %
BCS 260/4	$\leqslant 10$	2.2	6	15
336	28, 29*	31	7	12
337	22†	29	8	7
456	110	116	7	8
457	290	270‡	8	18
459	70	62	19	8
460	20	19	8	16
SRM 361	42	41	7	14
362	130	135	7	8
363	20§	16	8	8
364	340¶	337‡	7	7
365	<0.5‖	0.65	11	9
JK1C	2.1‖; 1, 2*	1.3	12	23

* The figures shown were obtained by Frech.[9]
† Result obtained by Burke.[15]
‡ Si was added to the core prior to addition of the samples because Si:Sb $< 5:1$.
§ Certificate value for SRM 1263; SRM 363 is the same material in the form of chips.
¶ Certificate value for SRM 1264; SRM 364 is the same material in the form of chips.
‖ Single result quoted on the certificate.
All other figures in the second column are certificate values.

With the other elements, straight-line calibration graphs passing through the origin were obtained for indium, thallium, selenium, telluriun and cadmium. The calibration graph for tin passed through the origin but was curved towards the mass axis, particularly for masses of tin in excess of 2.5 μg. The calibration graph for zinc was extensively curved because of the high degree of damping necessary to keep the apparent absorbances below 1.0. From these graphs the mass for 1% absorption was obtained in each instance. These data are shown in Table VI.

TABLE VI

MASSES REQUIRED FOR 1% ABSORPTION FOR VARIOUS ELEMENTS

Element	In	Tl	Sn	Se	Te	Zn	Cd
Mass for 1% absorption/ng	~0.7	0.14	46	12	0.18	0.043	~0.11

Discussion

Steel JK2C has not been fully standardised for the amount of antimony it contains, but contents of 32 and 27 $\mu g\ g^{-1}$ are reported on the certificate and Frech[9] has found antimony concentrations of 27 and 29 $\mu g\ g^{-1}$. The average value of 29 $\mu g\ g^{-1}$ was selected as the antimony content of this steel. Steel BCS 328 has been fully standardised and contains 260 $\mu g\ g^{-1}$ of antimony.

The accuracy of the results for antimony shown in Table V is considered to be good, the agreement between our results and those for standardised steels being very satisfactory. The precision of the method is acceptable, although not so good as that for a similar method for lead reported previously.[13] This is probably because, in this study, the furnace was usually operated at a temperature in the range 2550–2640 °C, which is about the maximum temperature that can be achieved with the equipment already described.[11] Corrosion of the graphite surfaces of the furnace, from trace amounts of reactive gases left in the argon stream and from air not completely removed from the graphite during the heating-up procedure, is more noticeable at higher temperatures and this leads to more scatter in the results.

Lundberg and Frech[16] have reported that scatter due to inhomogeneity should not be the major contribution to the relative standard deviation when milligram masses of steel are analysed for antimony by adding turnings to a furnace.

For the first time since using this design of induction furnace, a matrix effect has been observed for the determination of an element in steel. Steels BCS 457 and SRM 364 produced consistently high results for antimony when added to the normal graphite core. Both alloys were analysed on four different occasions using five or more samples each time and the average results were 449 $\mu g\ g^{-1}$ for BCS 457 and 521 $\mu g\ g^{-1}$ for SRM 364. A close examination of the chemical composition of all the steels, which had been added to the core, showed that BCS 457 and SRM 364 were exceptional only in that the ratios of the concentrations of silicon to antimony were low at 1.6:1 and 2.6:1, respectively, while in all other instances, the ratios were in excess of 6:1. It was felt that the presence of silicon must have reduced the rate of diffusion of antimony in molten steels, when the ratio of silicon to antimony was in excess of 5:1, such that the rate of release of antimony into the gas phase was diminished. It was decided to add silicon powder to the graphite core in order to ensure that the ratio of silicon to antimony in the molten metal was in excess of 5:1 and when this was done, acceptable results were obtained for BCS 457 and SRM 364 as reported in Table V. Incidentally, steels with a silicon to antimony ratio of less than 5:1 are unusual so the need to add silicon to a core will occur very occasionally.

The atomic-absorption spectrophotometer was operated without a background corrector. To check that there was negligible molecular absorption and negligible light scattering from relatively high concentrations of the elements present in steels that are volatile at high temperatures, the instrument was peaked up at 231.1 nm using the antimony hollow-cathode lamp, which was then replaced with a deuterium lamp, and samples of Specpure manganese (Johnson Matthey & Co. Ltd.), JK2C, BCS 457 and SRM 364 were added to the furnace core at 2540 °C. In no instance was there an absorbance reading in excess of 0.01 unit. Manganese is present in almost all steels and boils at 1962 °C.

The limit of detection of the method is 0.12 $\mu g\ g^{-1}$ of antimony and was taken as twice the standard deviation for sample SRM 365. This limit of detection is lower than any other reported in Table I.

Over a period of 4 years a considerable amount of data has been accumulated on the determination of trace elements in steels using atomic-absorption spectrophotometry with the introduction of solid samples into a constant-temperature induction furnace and an assessment of the real value of the method can now be given. Detailed results have already been reported for bismuth,[11] silver[12] and lead[13] in irons and steels, and have just been given for antimony in irons and steels. The method can be applied to the determination of many trace elements that are sufficiently volatile at 2600 °C or lower temperatures. These elements include indium, thallium, tin, lead, antimony, bismuth, selenium, tellurium, silver, zinc and cadmium, for which calibration graphs have been obtained. In theory the method should also be suitable for the determination of trace concentrations of magnesium, calcium, aluminium, gallium, manganese and copper in steels. However, the method is so sensitive that appreciable background absorption from magnesium, aluminium, manganese and copper continuously released from the graphite core has been obtained by us even using vacuum-degassed USP grade graphite. Suitable calibration graphs for very low masses of these elements have not yet been obtained. Gallium should present no problems with respect to background absorption.

The masses required for 1% absorption for various elements have already been reported in this paper (see Results). In Table VI the sensitivity for zinc is for a damped signal and the mass for 1% absorption in the absence of damping will be considerably less than 43 pg. The results for indium and cadmium may well be significantly in error. The indium content of the nickel-base alloy R3387 used to construct the calibration graph is nominally 10 $\mu g\ g^{-1}$ but could be appreciably lower. The cadmium content of JK2C is given as 0.03 $\mu g\ g^{-1}$ on the certificate, from a single determination, but this figure seems to be too high because the mass for 1% absorption would be expected to be similar to that for zinc.

The reliable masses for 1% absorption for the elements reported here along with those for bismuth,[11] silver[12] and lead,[13] reported earlier, have been converted into concentrations for 10-mg samples and are shown in Table VII. Also shown in this table are the concentrations of these elements in solution ($\mu g\ ml^{-1}$) producing 1% absorption in an air - acetylene flame,

using the same resonance lines for the elements as for the furnace work,[17] and these concentrations converted into $\mu g\ g^{-1}$ for steels assuming that 2 g of steel are dissolved in 100 ml of solution in each instance.

The results shown in Table VII are very interesting. At the furnace temperatures employed, all these elements are monatomic in the vapour phase.[18] In the air - acetylene flame with a temperature of about 2300 °C, all these elements with the exception of tin should exist mainly in the monatomic form. Tin will be present both as the monatomic form and as the monoxide.[19] It will be noticed that the *C/A* values for thallium, lead, bismuth, tellurium and silver are all between 1300 and 1800 while those for tin, antimony and selenium are much lower. Admittedly the sensitivities reported in column *A* were not all obtained at the temperature of the air - acetylene flame; the sensitivity increases with increasing temperature. For example, 1 μg of lead from BCS 327 gave absorbances of 0.15 and 0.27 at 2010 °C and 2150 °C, respectively,[13] and 20 ng of tellurium from SRM 361 gave an absorbance of 0.29 at 2190 °C and of 0.59 at 2350 °C. However, if all the results in column *A* had been obtained at the temperature of the air - acetylene flame, then the *C/A* values for thallium, lead, bismuth, tellurium and silver would have been in excess of 1000 and those for tin, antimony and selenium would have been lower than those reported in Table VII.

TABLE VII

DATA ON CONCENTRATIONS FOR 1% ABSORPTION OBTAINED BY ADDING SOLID SAMPLES TO AN INDUCTION FURNACE AND FROM NEBULISING 2% *m/V* SOLUTIONS OF STEELS INTO AN AIR - ACETYLENE FLAME

Element	Resonance line/nm	Furnace temperature/ °C	Concentration for 1% absorption			*C/A*
			*A**/ $\mu g\ g^{-1}$	*B*†/ $\mu g\ ml^{-1}$	*C*‡/ $\mu g\ g^{-1}$	
Thallium	276.8	2330	0.014	0.5	25	1786
Tin	286.3	2450	4.6	3.5	175	38
Lead	283.3	2000	0.017	0.5	25	1471
Antimony	231.1	2630	0.14	1.1	55	393
Bismuth	306.8	2070	0.015	0.5	25	1667
Selenium	196.0	2430	1.2	0.5	25	21
Tellurium	214.3	2350	0.018	0.5	25	1389
Silver	328.1	2270	0.0018	0.06	3	1667

* Using induction furnace.

† Following dissolution of steel in acid and atomisation in an air - acetylene flame, assuming that the sensitivities are the same in the presence and absence of iron.

‡ After converting $\mu g\ ml^{-1}$ into $\mu g\ g^{-1}$ of steel.

These *C/A* values of approximately 1500 in Table VII are found for the elements that quickly diffuse out of the molten globule of steel into the gas phase within our induction furnace. These are also the elements that should be readily removed from steel on vacuum melting. Indeed, Chernov and Ageev[20] reported that lead and bismuth were readily removed from iron on vacuum induction melting, tin and antimony were removed more slowly and arsenic was not removed at all. The boiling-points of the eight elements under discussion are shown in Table VIII. On boiling-point alone, tin should be the most difficult element to remove by vacuum melting or by volatilisation in our furnace but, intuitively, one would expect these elements, which show some non-metallic properties, to be held back in molten steel because of bonding between the elements and iron atoms. These elements include tin, antimony and selenium and, indeed for them, *C/A* values much less than 1000 were obtained. If tin were entirely monatomic in the air - acetylene flame, the sensitivity would be less than 175 $\mu g\ g^{-1}$ and the *C/A* value would be less than 38 as given in Table VII.

TABLE VIII

BOILING-POINTS OF VARIOUS TRACE ELEMENTS FOUND IN STEEL

Element	Tl	Sn	Pb	Sb	Bi	Se	Te	Ag
Boiling-point/°C	1457	2270	1740	1750	1560	685	990	2212

In this study, attempts were made to obtain a calibration graph for arsenic in steel - arsenic sublimes at 613 °C at atmospheric pressure, but without success. Even at 2570 °C there was no evidence for the presence of arsenic atoms in the gas phase, the absorbance being zero in each instance when milligram masses of steels containing arsenic were added to the graphite core through which the resonance line for arsenic at 193.7 nm was being passed.

The limits of detection for the elements that readily volatilise from steel have been estimated and are shown in Table IX. This was carried out as follows. For a single-beam atomic-absorption spectrophotometer such as the Perkin-Elmer 300S and an air - acetylene flame, the relative standard deviation of a determination is often approximately 1% when solutions are nebulised to give absorbances between 0.2 and 0.8. Under these conditions the limit of detection is frequently one fifth to one tenth of the concentration for 1% absorption. With our induction furnace the precision is poorer with a relative standard deviation of 5–10%, and hence one would reasonably expect a limit of detection about the same as the concentration for 1% absorption for a 10-mg sample. The estimated limits of detection in Table IX are taken as the concentrations for 1% absorption ($\mu g\ g^{-1}$) that have been given in Table VII (column *A*).

TABLE IX

ESTIMATED AND ACTUAL LIMITS OF DETECTION FOR TRACE ELEMENTS READILY VOLATILISED FROM STEELS

Element	Estimated limit of detection in steel/ $\mu g\ g^{-1}$	Actual limit of detection in steel/ $\mu g\ g^{-1}$
Thallium	0.014	—
Tin	4.6	—
Lead	0.017	$\leqslant 0.02$*
Antimony	0.14	0.12†
Bismuth	0.015	0.004‡
Selenium	1.2	—
Tellurium	0.018	—
Silver	0.0018	0.005§

* See reference 13.
† Reported in this paper.
‡ See reference 11.
§ See reference 12.

Considering the assumptions that have been made in the method for estimating the limit of detection, the agreement between actual and estimated limit of detection in the instances where actual limits have been determined, is reasonable. It can be said with certainty that the actual limits of detection for thallium and tellurium and also zinc and cadmium will be well below 0.1 $\mu g\ g^{-1}$ but that the limits of detection for tin and selenium at the temperatures given in Table VII will be not as good. Of course, the limits of detection for both tin and selenium may well be better at temperatures in excess of 2600 °C.

The determination of trace elements in metals by atomic-absorption spectrophotometry with the introduction of solid samples into electrically heated graphite furnaces has been shown to be convenient and reliable on many occasions.[11–13,21–24] There is evidence that introducing samples into a graphite furnace being maintained at constant temperature is to be preferred.[21] The furnaces may be inductively or resistively heated but the cost of the latter is cheaper, unless a spare induction generator is available. It is to be hoped that instrument manufacturers will soon provide graphite atomisers to which metal samples can be conveniently added at controlled constant temperatures. Facilities for measuring both peak height and peak area will also be desirable.

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DETERMINATION OF BISMUTH IN NICKEL-BASE ALLOYS BY ATOMIC ABSORPTION SPECTROMETRY WITH INTRODUCTION OF SOLID SAMPLES INTO AN INDUCTION FURNACE

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SUMMARY

Atomic absorption spectrometry with an induction furnace is applicable to the determination of bismuth at 0.02—10 $\mu g\ g^{-1}$ levels in 1—30-mg samples of nickel-base alloys dropped into the furnace. Calibration graphs of peak absorbance versus mass of bismuth are constructed by use of standardised alloys. Samples of alloys can be added to the furnace at 2.5-min intervals. Calibration graphs, accuracy, precision and limits of detection of the method are discussed for 26 alloys. Accuracy is assessed by comparing the induction furnace results with results supplied with the alloys, and with results obtained for solutions of the alloys by atomic absorption spectrometry in association with hydride generation or a mini-Massmann furnace. With alloys containing more than 0.1 $\mu g\ Bi\ g^{-1}$, relative standard deviations by the induction furnace method are usually < 15%. The limit of detection for bismuth is 0.02 $\mu g\ g^{-1}$

The hot ductility, workability and rupture life of nickel-base alloys are adversely affected by the presence of trace levels of bismuth as low as 0.3 $\mu g\ g^{-1}$ [1—4]. For this reason, stringent specifications have been set for the maximum concentration of bismuth in nickel-base alloys. For example, the SAE Aerospace Metal Specification (AMS) 2280 [5] lists the maximum permissible bismuth content as 0.5 $\mu g\ g^{-1}$, and the DIN 17 01 Preliminary Standard (1974) [6] stipulates a maximum bismuth concentration of 0.2 $\mu g\ g^{-1}$ for primary nickel.

The accurate determination of bismuth at such low concentrations is a challenging task for the metallurgical analyst. Methods that have been reported for the determination of bismuth in nickel-base alloys at concentrations less than 1 $\mu g\ g^{-1}$ are summarized in Table 1, which includes information on the limits of detection for each method.

Undoubtedly the most convenient and sensitive methods described in the literature for the determination of bismuth in nickel-base alloys are hollow-cathode emission spectrometry with solid samples [11] and atomic absorption spectrometry of metallic samples added directly to a resistively-heated graphite furnace [16]. However, Andrews and Headridge [17] have reported that bismuth can be determined in steels by the direct addition of metal turnings or millings (chips) to a constant-temperature induction furnace with

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TABLE 1

Methods for the determination of bismuth in nickel-base alloys

Method	Limit of detection for bismuth ($\mu g\ g^{-1}$)	Ref.
D.c. arc emission after preconcentration by precipitation of Bi_2S_3 in CuS	0.5	[7]
D.c. arc emission with LiF—AgCl carrier	0.5	[8]
D.c. arc emission after preconcentration by precipitation of Bi_2S_3 in MoS_3	0.1	[9]
D.c. arc emission of chips mixed with Li_2CO_3	0.2	[10]
Hollow-cathode emission spectrometry	0.02	[11]
Square-wave polarography after solvent extraction	0.5	[12]
Flame a.a.s. after solvent extraction	0.5	[12]
Flame a.a.s. after electrodeposition	0.1	[13]
A.a.s. with graphite furnace atomization after dissolution of alloy	0.1	[14]
A.a.s. following hydride generation	0.1	[15]
A.a.s. of chips in graphite furnace	0.02	[16]

a limit of detection of 0.004 $\mu g\ g^{-1}$, and this method has now been adapted to the determination of bismuth in nickel-base alloys. The accuracy of the method was assessed by comparing the results with those obtained from solutions of the alloys by atomic absorption spectrometry after hydride generation and after atomization in a mini-Massmann furnace, and with those obtained by independent analyses.

EXPERIMENTAL

Materials

Standardized nickel-base alloys were supplied by Henry Wiggin and Co. Ltd., Rolls Royce Ltd. (Derby and Filton) and Ross and Catherall, Ltd.

Apparatus and method for obtaining absorbances for a series of solid samples

These were identical to those previously described [17] except that the graphite core and side arms were made from AGTS Grade Graphite (British Acheson Electrodes) and the flow rate of the stir gas was 0.08 $dm^3\ min^{-1}$. Graphite cores and side arms were baked under vacuum for 30 min at ca. 1500°C before use. The resonance line at 306.8 nm from a bismuth hollow-cathode lamp (Pye-Unicam) was used with a slit width of 0.2 nm on a Perkin-Elmer 300 S atomic absorption spectrometer. When samples within the concentration range of 0.02—10 μg Bi g^{-1} were handled, the masses of samples added to the furnace lay within the range 1—30 mg and were determined with a 5-place balance. The core temperature was 2250°C. For the determination of bismuth at concentrations below 1.1 $\mu g\ g^{-1}$, × 2 or × 5 scale expansion was used on the 300 S for samples and standards.

Calibration graphs

For the determination of bismuth in nickel-base alloys containing 0.3—10 μg Bi g^{-1}, calibration graphs of peak absorbances versus amount of bismuth were obtained by dropping increasing amounts of alloy R 3386 (2.0 μg Bi g^{-1}) into the graphite core under conditions capable of producing absorbances up to 1.0. For nickel-base alloys containing < 1.0 μg Bi g^{-1}, calibration graphs were prepared in a similar way with alloys R 3385 (0.98 μg Bi g^{-1}) or RRF1 (0.61 μg Bi g^{-1}), which were standardized against alloy R 3386.

Procedures for the determination of bismuth in nickel-base alloys

Induction furnace method. When a series of nickel-base alloys is to be analysed, suitable masses are dropped into the graphite core over a period of 2—3 h; during the same run but generally at the start of the run, various masses of R 3385, R 3386 or RRF 1 are also added for the purpose of constructing a calibration graph. When the run is completed, the calibration graph is drawn and the mass of bismuth in each sample is obtained from the graph. The concentrations of bismuth in the samples are then calculated.

Hydride generation method. A method similar to that of Drinkwater [15] was used. The hydride was dissociated to bismuth atoms within a quartz tube (8 mm i.d. × 17.5 cm long) heated electrically and maintained at a temperature of ca. 900°C. A Unicam SP90A atomic absorption spectrometer and the bismuth resonance line at 223.1 nm were employed. Calibration graphs of peak absorbance versus ng of bismuth were prepared by adding known masses of bismuth to a solution of alloy DTA which was known to contain very little bismuth.

Graphite tube method. A method similar to that of Welcher et al. [14] was employed. The alloys were dissolved in concentrated hydrofluoric acid—concentrated nitric acid—water (1:3:5, v/v) to give 1% or 2% (w/v) solutions of metal. Aliquots (5 μl) were pipetted into the Varian CRA 63 tube furnace to obtain peak absorbances at the bismuth resonance line (223.1 nm). A hydrogen background corrector was used. The bismuth concentrations in these solutions were determined by a standard additions method.

RESULTS

The resonance line at 306.8 nm was employed to construct calibration graphs for 0—65 ng of bismuth for the determination of bismuth between 0.02 and 10 μg g^{-1} with the induction furnace. These calibration graphs were straight lines through the origin. The mass of bismuth producing 1% absorption was approximately 0.3 ng.

Several series of nickel-base alloys were dropped into the furnace to determine their bismuth contents under the conditions outlined in the Experimental Section. The results (Table 2) indicate that the relative standard deviations are usually less than 15%, when the alloys contain more than 0.1 μg Bi g^{-1}. The limit of detection, defined as twice the standard deviation of several series of samples producing absorbances between 0.01 and 0.03, was 0.02 μg Bi g^{-1}.

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TABLE 2

Results for the determination of bismuth in nickel-base alloys

Alloy	Induction furnace			BiH_3	CRA 63	Company result
	Bi found ($\mu g\ g^{-1}$)	No. of samples analysed	R.s.d. (%)	Bi found ($\mu g\ g^{-1}$)	Bi found ($\mu g\ g^{-1}$)	Bi content ($\mu g\ g^{-1}$)
RRF2	1.9	5	8	1.7	1.8	1.9[e]
TT3	2.9	6	11	2.2	3.1	2.9[f]
TT4	5.8	6	6	5.4	4.7	7[f]
TT5	8.1	6	10	7.4	6.9	10[f]
DTB	2.5	6	9	2.4	2.1	2.5[g]
DTC	5.7	8	17	6.2	5.1	5.8[g]
DTD	6.7	8	9	6.2	5.8	6.6[g]
DTE	7.9	7	19	7.1	7.0	8.0[g]
DTF	10.2	7	11	10.1	9.3	10[g]
R 3387	8.5	8	9	8.4	7.1	8.5[g]
R 3388	3.9	7	10	3.6	3.0	3.9[g]
R 6286	9.9	8	6	8.3	9.7	9.0[g]
R 7248[a]	6.0	8	4			5.3[g]
RRF1	0.61	8	18	0.5	0.6[d]	0.5[e]
TT2	0.78	8	12		0.7	0.9[f]
	0.82[c]	8	9			
DTA	0.03[b]	8	39			<0.2[g]
	0.05[c]	8	30			
R 3385	0.98	8	7	0.8	0.9[d]	1.0[g]
	0.99[c]	8	14			
R 6285	0.83	7	11	0.5	0.8	0.9[g]
	0.79[c]	8	15			
R 6287	0.11[b]	8	10	<0.2		<0.2[g]
R 7247[a]	0.56	8	10			0.5[g]
BCS 310	0.24[b]	7	12	<0.2		<0.5[g]
BCS 310/1	0.17[b]	7	9	<0.2		<0.5[g]
ST1	0.39	7	6	0.3	0.4	0.30[h]
	0.35[c]	8	12			
ST2	0.96	8	11	0.9	0.8	0.78[h]
	1.01[c]	7	5			
ST3	1.42	8	11	1.4	1.3	1.07[h]
	1.35[c]	11	13			
TT1	0.02[b]	8	32			<0.1[f]
R 3386	-	-	-	2.0	1.6	2.0[g]

[a] Iron-base alloys containing about 30% nickel. [b,c] R 3386 was used as a standard for constructing the calibration graphs except for the alloys marked[b] and [c] where R 3385 and RRF1 were used, respectively. [d] Without background correction. [e] By a.a.s. after hydride generation. [f] By hollow-cathode emission. [g] By square-wave polarography after solvent extraction. [h] By electrothermal atomization of solutions in the CRA 63 cup.

Results for the determination of bismuth in these alloys by atomic absorption after hydride generation are also shown in Table 2. For these results, duplicate samples of the alloys were taken into solution. The peak

absorbances from three aliquots of each solution were averaged and the average absorbances converted to masses of bismuth from a calibration graph. The calculated results of bismuth concentration from the two dissolved samples were then averaged. A statistical assessment of the results indicated that the limit of detection was 0.2 $\mu g\ g^{-1}$.

Results for the determination of bismuth by electrothermal atomization of bismuth from solutions of the alloys are also presented in Table 2. These results are the average of two determinations of the bismuth in 5-μl aliquots of solution, obtained by a single dissolution of each alloy, based on peak absorbances and standard additions.

DISCUSSION

Alloy R 3386 was selected as a reliable standard because it has been stated to contain 2.0 $\mu g\ Bi\ g^{-1}$ and 1.9 $\mu g\ Bi\ g^{-1}$ when analysed by square-wave polarography after solvent extraction and by hollow-cathode emission spectrometry, respectively. Its bismuth content was taken as 2.0 $\mu g\ g^{-1}$ for induction furnace work.

There is good agreement between company results and those obtained on the induction furnace (Table 2) except for samples TT4 and TT5, where all three methods employed in this work indicate that the company results were too high. The results obtained for the bismuth contents of alloys R 7247 and R 7248 with the induction furnace are probably slightly high, because these alloys are actually iron-base alloys containing ca. 30% of nickel, and bismuth is certainly released more readily from iron-base alloys than from nickel-base alloys at 2050°C, the temperature used in the preliminary investigations here. This resulted in a larger peak absorbance for the same mass of bismuth from a molten iron-base alloy than from a molten nickel-base alloy. The effect was very pronounced at 2050°C, the ratio of peak absorbances for the same mass of bismuth from iron- and nickel-base alloys being 4:3, and it is probably not completely eliminated at 2250°C, the temperature used for these determinations.

The results obtained here for samples ST1, ST2 and ST3 are slightly higher than those reported by the company. However, half the present results were based on a bismuth content of 0.61 $\mu g\ g^{-1}$ for alloy RRF1 which was used to prepare the calibration graph. If the company value of 0.5 for RRF1 is more correct and the bismuth contents of ST1, ST2 and ST3 are calculated on this value, then bismuth contents of 0.29, 0.83 and 1.11 $\mu g\ g^{-1}$ are obtained for ST1, ST2 and ST3, respectively, and these values are in good agreement with the company results.

The precision of the induction furnace method is acceptable for these very low concentrations. Relative standard deviations were seldom in excess of 15% when the bismuth content was more than 1 $\mu g\ g^{-1}$. Where higher relative standard deviations were obtained, e.g. 17% for DTC and 19% for DTE, it is suspected that there is a less homogeneous distribution of bismuth

in the samples. The limit of detection of 0.02 $\mu g\ g^{-1}$ could probably be improved further by using the 223.1-nm resonance line from a high-intensity hollow-cathode lamp. The 223.1-nm line from the Pye-Unicam hollow-cathode lamp used in this study was of relatively low intensity, and the 306.8-nm line was used instead.

The limit of detection for bismuth of 0.02 $\mu g\ g^{-1}$ is the same as that obtained by Marks et al. [16], who added chips to a Perkin-Elmer model HGA 2100 device. However, a much more extensive range of bismuth concentrations has been investigated in the present study.

The results obtained by hydride generation (Table 2) are usually slightly lower than those obtained with the induction furnace; the reason for this is not obvious. The limit of detection of 0.2 $\mu g\ g^{-1}$ is not so good as that obtained by Drinkwater [15] probably because the flask in which the hydride was generated was of greater volume and the optical path through the heated quartz tube was less than that used by Drinkwater.

The results obtained with the mini-Massmann furnace (Table 2) are generally also slightly lower than those obtained with the induction furnace. These slightly low results arise because the sensitivity of the method for bismuth falls by approximately 2% for each heating cycle of the furnace. It was our usual practice to spike solutions from alloys with x ng and $2x$ ng of bismuth and to analyse these in the following order: (i) alloy solution + $2x$ ng of bismuth in duplicate, (ii) alloy solution + x ng of bismuth in duplicate and (iii) alloy solution without bismuth addition in duplicate. The best straight line was then drawn through the averages of the duplicate results, and the intercept on the concentration axis was taken as the concentration of bismuth in the 5-μl aliquot of alloy solution. However, because of the decrease in sensitivity with each heating cycle, the calibration graph should actually be a slight curve with an intercept about 10% further along the concentration axis from the origin. The shape of this curve will vary slightly from one alloy to another and it is only practical to extrapolate a straight line. For this reason, the results by the mini-Massmann method will be about 10% low. If these results are raised by 10%, they are in quite good agreement with the results obtained with the induction furnace and with the results from the companies. With hindsight, this drop in sensitivity leading to curvature in the graph could have been corrected for, by adding the solutions in the order (i), (ii), (iii), (iii), (ii), (i),and drawing the best straight line through the averages of the duplicate results. The limit of detection of the mini-Massmann method was 0.1 $\mu g\ g^{-1}$, taken as twice the signal to noise ratio.

Of the three methods investigated, the induction furnace method seems preferable, as it does not require dissolution of the alloy samples and has a much better limit of detection. However, a reliable nickel-base standard is necessary before the method can be used reliably.

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DETERMINATION OF SILVER AND THALLIUM IN NICKEL-BASE ALLOYS BY ATOMIC ABSORPTION SPECTROMETRY WITH INTRODUCTION OF SOLID SAMPLES INTO AN INDUCTION FURNACE

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SUMMARY

Atomic absorption spectrometry with an induction furnace is used for the determination of silver (0.03—12 $\mu g\ g^{-1}$) and thallium (0.004—12 $\mu g\ g^{-1}$) in 1—40-mg samples of nickel-base alloys dropped into the furnace. Calibration graphs of peak absorbance versus mass of element were constructed by use of standardised alloys. The accuracy, precision and limits of detection of the method are described for numerous nickel-base alloys. With alloys containing more than 0.2 μg Ag g^{-1} and 0.4 μg Tl g^{-1}, relative standard deviations are usually <15% and <12%, respectively. The limits of detection for silver and thallium are 0.014 $\mu g\ g^{-1}$ and 0.004 $\mu g\ g^{-1}$, respectively.

It is well known that elements that have low melting points and low solubility in nickel have deleterious effects on the properties of nickel-base alloys such as hot workability and stress-rupture life [1, 2]. These elements include thallium, tin, lead, arsenic, antimony, bismuth, sulphur, selenium, tellurium, silver, cadmium and zinc [3]. In this paper, methods will be described for the determination of silver and thallium in nickel-base alloys. Stringent specifications stating the maximum concentrations of silver, thallium and other elements in nickel-base alloys have been published [1, 2]. These concentrations are very low and can be less than 1 $\mu g\ g^{-1}$. Refined nickel is the base metal for such alloys and the specification for grade R. 99.95B (BCS 375:1977) states that the concentrations of silver and thallium should not exceed 1 $\mu g\ g^{-1}$ and 0.2 $\mu g\ g^{-1}$, respectively. Ideally, the limits of detection for the analytical methods used to determine these elements should be $\leqslant 0.1\ \mu g\ g^{-1}$ for silver and $\leqslant 0.02\ \mu g\ g^{-1}$ for thallium.

Sensitive methods that have been reported for the determination of silver and thallium in nickel-base alloys are shown in Table 1 along with their limits of detection. For silver, methods I, III, V, VI and VII have the required sensitivity for the analysis of refined nickel. However, methods III and VII are the more attractive because preconcentration steps are time-consuming and could lead to the pick-up of minute traces of silver from reagents. For thallium, only methods III and VIII have limits of detection approaching 0.02 $\mu g\ g^{-1}$ for refined nickel.

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TABLE 1

Methods for the determination of silver and thallium in nickel-base alloys

Method	Limit of detection ($\mu g\ g^{-1}$)		Ref.
	Silver	Thallium	
I D.c. arc emission spectrography (preconcentration on CuS)	0.1	1	4
II D.c. arc emission spectrography (preconcentration on MoS_3)	0.2	0.2	5
III Hollow-cathode emission spectrometry	$\leqslant 0.01$	~ 0.05	6
IV Spark-source mass spectrometry	0.15	0.15	3
V A.a.s. (ion-exchange preconcentration)	~ 0.001		7
VI A.a.s. after solvent extraction	0.02		8
		0.1	9
VII A.a.s. after alloy dissolution[a]		0.1	10,11
	0.1	0.2	12
	0.005		13
VIII A.a.s. of chips[a]		0.03	14

[a]With graphite furnace atomization.

Headridge and co-workers have already used atomic absorption spectrometry for the determination of bismuth [15], silver [16], lead [17] and antimony [18] in steels and bismuth [19] in nickel-base alloys with the introduction of solid samples into an induction furnace. A similar procedure has been applied to the determination of silver and thallium in nickel-base alloys and is now described.

EXPERIMENTAL

Materials

Analysed nickel-base alloys were supplied by Henry Wiggin and Co. Ltd., the National Physical Laboratory, Rolls-Royce Ltd. (Derby and Filton) and Ross and Catherall, Ltd. Samples for analysis should preferably be millings or turnings so that no more than three pieces need be added to the furnace core at the same time. Millings and turnings should be degreased with a suitable solvent before use.

Apparatus and measurement procedure for a series of solid samples

These were identical to those previously described [15] except that the graphite core and side arms were made from AGTS-grade graphite (British Acheson Electrodes) and the flow rates of the purge and stir gas were as follows: for silver, purge gas 2 l min^{-1}, stir gas 75 ml min^{-1}; for thallium, purge gas 100 ml min^{-1}, stir gas 50 ml min^{-1}. Graphite cores and side arms were baked under vacuum for 12 h at ca. 1800°C before use. Absorbance measurements were made on a Perkin-Elmer 300S atomic absorption spectrometer using a silver (Activion) or thallium (Perkin-Elmer) hollow-cathode

lamp. The masses of samples added to the furnace were determined with a 5-place balance. The experimental conditions for the determinations of silver and thallium are shown in Table 2.

Calibration graphs

For the determination of silver in nickel-base alloys containing 0.25—11 μg Ag g^{-1}, calibration graphs of peak absorbance versus amount of silver were obtained by dropping increasing amounts of alloy R 3386 (2.2 μg Ag g^{-1}) into the graphite core under conditions capable of producing absorbances up to 1.0. For the nickel-base alloy containing <0.25 μg Ag g^{-1}, the calibration graph was prepared in a similar way with alloy R 6287 (0.25 μg Ag g^{-1}), which was standardised against alloy R 3386.

For the determination of thallium in nickel-base alloys containing 0.4—12 μg Tl g^{-1}, calibration graphs of peak absorbance versus amount of thallium were obtained by dropping increasing amounts of alloy ST3 (2.2 μg Tl g^{-1}) into the graphite core. For the nickel-base alloys containing <0.6 μg Tl g^{-1}, calibration graphs were prepared in a similar way with alloy R 6285 (0.71 μg Tl g^{-1}) which was standardised against alloy ST3.

Procedure for the determination of silver and thallium in nickel-base alloys

When a series of nickel-base alloys is to be analysed, suitable masses are dropped into the graphite core over a period of 2—3 h; during the same run but generally at the start of the run, various masses of R 3386 or R 6287 (for silver) or of ST3 or R 6285 (for thallium) are also added for the purpose of constructing a calibration graph. When the run has been completed, the calibration graph is drawn and the mass of silver or thallium in each sample is obtained from the graph. The concentrations of silver or thallium in the samples are then calculated.

TABLE 2

Experimental conditions for the determination of silver and thallium

Concentration range (μg g^{-1})	Mass range of sample (mg)	Core temp. (°C)	Wavelength (nm)	Slit width (nm)	Scale expansion
Silver					
5—11	0.7—2.5	2300	338.1	0.2	× 1
1—5[a]	1—7	2300—2350	328.1	0.2	× 1
0.25—1	3—12	2350	328.1	0.2	× 1
<0.25	6—12	2300	328.1	0.2	× 5
Thallium					
8—12	2—5	2530	238.0	0.2	× 1
0.6—8	2—20	2400—2530	377.6	0.7	× 1
<0.6	5—40	2450—2540	276.8	0.7	× 4 to × 10

[a]When necessary, damping position 3 can be used with this range to keep the highest absorbances below 1.0. Otherwise damping position 1 is employed. Damping positions 1 and 3 are for time constants of 0.2 and 3 s, respectively.

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RESULTS AND DISCUSSION

The calibration graphs for silver were straight lines through the origin over the ranges specified above. Calibration graphs for thallium were straight lines through the origin up to 15 ng of thallium but curved over slightly towards the concentration axis above this mass. From typical graphs the masses of silver producing 1% absorption were calculated as 47 pg and 80 pg at 2300°C using the 328.1 and 338.1-nm resonance lines, respectively. The masses of thallium producing 1% absorption were 41, 118 and 400 pg at 2500°C using the 276.8 377.6 and 238.0-nm resonance lines, respectively. Results for the determination of silver in 17 nickel-base alloys and thallium in 30 such alloys are shown in Tables 3 and 4.

For silver, alloy R 3386 was selected as a reliable standard because it has been stated to contain 2.2 μg Ag g^{-1} when analysed both by hollow-cathode emission spectrometry and by atomic absorption spectrometry with flame atomisation directly on a solution of the alloy [3]. For thallium, alloy ST3 was employed as a standard because it has been reported to contain 2.16 μg Tl g^{-1} when analysed by electrothermal atomic absorption spectrometry on solutions and 2.28 μg Tl g^{-1} by hollow-cathode emission spectrometry. The average value of 2.2 μg Tl g^{-1} was taken for this alloy.

The results for silver are considered to be quite good with satisfactory

TABLE 3

Results for the determination of silver in nickel-base alloys

Alloy	Silver found (μg g^{-1})	No. of samples analysed	Relative standard deviation (%)	Company result (μg g^{-1})
DTA	0.03	5	22	<1.0[a]
R 6287	0.25	6	11	<1.0[a]
ST1	1.0	6	8	0.8[b]
ST2	2.7	6	7	2.7[b]
ST3	1.3	6	10	1.0[b]
DTB	2.1	6	8	1.9[a]
DTC	3.9	5	8	3.7[a]
DTD	5.0	5	9	4.8[a]
R 3385	1.2	6	5	1.2[a]
R 6285	1.2	12	9	1.6[a]
DTE	6.8	16	19	6.7[a]
DTF	11.2	20	13	9.1[a]
R 3387	9.8	5	11	9.8[c], 10[a]
R 3388	5.7	11	17	5.0[a], 5.0[c]
R 6286	10.5	4	14	10[a]
RRF 1	6.6	6	8	7.2[b]
RRF 2	10.9	4	12	9.5[b]

[a]By direct atomic absorption with an air—acetylene flame. [b]By electrothermal atomization of solutions. [c]By hollow-cathode emission.

TABLE 4

Results for the determination of thallium in nickel-base alloys

Alloy	Thallium found ($\mu g\ g^{-1}$)	No. of samples analysed	Relative standard deviation (%)	Company result ($\mu g\ g^{-1}$)
CSA2	0.004	6	14	<0.5[a], <0.2[b]
CSB2	0.008	12	28	<0.5[a], <0.2[b]
CSC2	0.006	6	39	<0.5[a], <0.2[b]
CSD2	0.005	5	12	<0.5[a], <0.2[b]
CSE2	0.005	9	33	<0.5[a], <0.2[b]
CSF2	0.005	11	23	<0.5[a], <0.2[b]
CSG2	0.004	5	44	<0.5[a], <0.2[b]
CSH2	0.005	6	20	<0.5[a], <0.2[b]
CSJ2	0.006	6	11	<0.5[a], <0.2[b]
CSK2	0.013	5	17	<0.5[a], <0.2[b]
CSW2	0.45	12	8	0.6[a]
CSZ2	0.037	6	14	<0.2[a]
R 6285	0.71	12	10	1[e]
R 6286	4.0	6	4	10[e]
R 3385	0.71	6	3	0.7[c]
R 3386	1.4	5	2	1.4[c]
R 3387	6.6	6	6	6.6[c]
R 3388	3.3	6	5	3.5[c]
RRF2	4.5	6	7	4.1[d]
TT2	3.6	12	6	5.5[b]
CSL2	2.1	6	6	2.5[a], 2.5[b]
CSM2	6.2	5	11	6.0[a], 6.0[b]
CSN2	3.2	6	11	3.0[a], 3.0[b]
CSO2	6.9	6	10	7.0[a], 7.0[b]
CSX2	2.4	6	3	2.6[a]
ST1	0.79	6	1	0.82[d]
ST2	0.70	12	7	0.84[d]
TT3	8.5	6	5	11[b]
TT4	10.4	6	4	14[b]
CSP2	11.8	6	3	12.5[a], 12.0[b]

[a]By electrothermal atomization of solutions in a carbon tube furnace. [b]By hollow-cathode emission. [c]By flame atomic absorption after solvent extraction. [d]By electrothermal atomization of solutions in the CRA 63 cup. [e]Nominal value.

agreement between the present results and the company results except for alloy DTF. Relative standard deviations are less than 15% except for alloy DTA which contains very little silver and for alloys DTE and R 3388 which have been analysed more frequently than normal to establish results of reasonable accuracy. There may be a more inhomogeneous distribution of silver in these last two alloys.

From the results for sample DTA in Table 3 the standard deviation is calculated as 0.007 μg Ag g^{-1} and the limit of detection is therefore 0.014 μg Ag g^{-1}. An identical result was obtained when a further nine samples of this alloy were analysed in a separate run. Almost certainly this limit of detection

would have been lower if a sample containing less than 0.03 μg Ag g^{-1} had been available for analysis.

The results for thallium are very satisfactory with good agreement between the present results and the company results except for samples TT2, TT3 and TT4; these were from an early series of nickel-base alloys for whch less accurate company results were available. For thallium concentrations in excess of 0.4 μg g^{-1}, relative standard deviations are less than 12%. The limit of detection being defined as twice the standard deviation for results for alloys containing very low concentrations of thallium was estimated to be 0.004 μg g^{-1} after examination of the results for the nine alloys CSA2 to CSJ2.

These limits of detection for silver and thallium are well below the limits sought as mentioned in the introduction, namely 0.1 μg g^{-1} for silver and 0.02 μg g^{-1} for thallium. Undoubtedly this method of atomic absorption spectrometry with the introduction of solid samples to an induction furnace is among the most sensitive available for the determination of silver and thallium in nickel-base alloys.

In previous studies on the determination of bismuth [15], silver [16] and antimony [18] in steels, it was shown that there was virtually no molecular absorption nor absorbance associated with resonance-light scatter from relatively high concentrations of volatile minor elements such as manganese. Therefore there was no need for the use of a background corrector. In this study, light of band width 0.2 nm from a deuterium lamp at the wavelengths 328.1 and 338.1 nm for silver and 238.0, 276.8 and 377.6 nm for thallium (i.e. the resonance lines of silver and thallium) was used to check for background absorption when nickel-base alloys were added to the induction furnace at the appropriate temperatures. In no instance was an absorbance in excess of 0.01 detected.

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DETERMINATION OF BISMUTH, LEAD AND TELLURIUM IN COPPER BY ATOMIC ABSORPTION SPECTROMETRY WITH INTRODUCTION OF SOLID SAMPLES INTO AN INDUCTION FURNACE

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SUMMARY

Atomic absorption spectrometry with an induction furnace is used for the determination of bismuth (0.015—10 $\mu g\ g^{-1}$), lead (0.2—15 $\mu g\ g^{-1}$) and tellurium (0.04—5 $\mu g\ g^{-1}$) in 2—30-mg samples of copper and low-alloy copper dropped into the furnace. Calibration graphs of peak area versus mass of element were constructed by use of standardised alloys. The accuracy, precision and limits of detection of the method are described for numerous copper samples. With alloys containing more than 0.1 μg Bi g^{-1}, 0.2 μg Pb g^{-1} and 0.8 μg Te g^{-1}, average relative standard deviations are 7%, 6% and 8%, respectively. The limits of detection for bismuth, lead and tellurium are 0.01, 0.1 and 0.02 $\mu g\ g^{-1}$, respectively.

Antimony, arsenic, bismuth, selenium and tellurium, and, to a lesser extent, lead, markedly affect the annealability of copper used in wire production and can exert harmful effects at levels below 1 $\mu g\ g^{-1}$ [1—4]. Trace levels of these same impurities are also known to affect the electrical conductivity of copper but generally this happens at levels above those at which they affect the annealability. For example, lead is known to impair electrical conductivity at a concentration of 8 $\mu g\ g^{-1}$. Therefore there is a need to determine these trace elements at concentrations below 10 $\mu g\ g^{-1}$ and often below 1 $\mu g\ g^{-1}$. A method is required of good accuracy and reasonable precision with a limit of detection for bismuth, lead and tellurium of 0.1 $\mu g\ g^{-1}$ or better.

Many papers have been published on the determination of these trace elements in copper; a selection of the methods used is given in Table 1. It can be seen that the methods involving anodic stripping voltammetry and atomic absorption spectrometry (a.a.s.) with hydride generation or using a graphite cup atomizer have the required sensitivity, but these are all methods involving a preconcentration step. Furnace a.a.s. after dissolution, but without preconcentration, is not quite sensitive enough. However, a.a.s. with the introduction of solid copper samples into a constant-temperature induction furnace has the required sensitivity and is the method reported in this paper. The induction furnace is similar to that used by Headridge and coworkers for the determination of bismuth [19], lead [20], silver [21] and antimony

TABLE 1

Methods for the determination of bismuth, lead and tellurium in copper

Method	Limit of detection ($\mu g\ g^{-1}$)			Ref.
	Bi	Pb	Te	
Emission spectrography with a globule arc	0.2	0.1	2	5
Inductively-coupled plasma spectrometry after dissolution		9		6
Molecular absorption spectrometry:				
after solvent extraction	1			7
after $Fe(OH)_3$ collection	<0.04			8
after $Fe(OH)_3$ collection and solvent extraction			1	9
Anodic stripping voltammetry:				
after electrolytic deposition of Cu		0.1		10
after ion exchange	0.004		0.02	11, 12
Atomic absorption spectrometry:				
after collection on $La(OH)_3$ and hydride generation	0.002		0.004	13, 14
furnace, after dissolution	0.2	0.4	0.2	15—17
graphite cup, after collection on $Fe(OH)_3$	0.02	0.1	<0.04	18

[22] in steels, and of bismuth [23], and silver and thallium [24] in nickel-base alloys. A review of the determination of volatile trace elements in metals by a.a.s. with the introduction of solid samples into furnaces ~~has been~~ published ~~recently~~ [25]. will be soon

EXPERIMENTAL

Materials

Standard copper samples and dilute copper alloys were obtained from the Canada Centre for Mineral and Energy Technology (CANMET) and Johnson Matthey Chemicals Ltd., respectively. Analysed copper samples were supplied by BICC Metals Ltd. Samples for analysis should preferably by chips so that no more than three pieces need to be added to the furnace core at the same time. Chips should be degreased with a suitable solvent before use.

Apparatus and measurement procedure for a series of solid samples

These were identical to those previously described [19] except that the graphite core and side arms were made from Ultra F purity graphite type UF-4S (Ultra Carbon, U.S.A.) for bismuth and tellurium, and from nuclear-grade graphite (British Acheson Electrodes Ltd.) for lead; also the window mounts were modified so that a continuous flow of argon from six radial holes was directed onto the windows to minimise metal deposition on their surfaces. This is known as the window gas. It is only used in conjunction with the purge gas. The furnace temperatures and gas flow rates used are shown in Table 2.

TABLE 2

Experimental conditions for the induction furnace

Element determined	Core temp. (°C)	Flow rates of argon (ml min^{-1})		
		Purge gas	Stir gas	Window gas
Bismuth	2400	150	40	1500
Lead	2380	200	40	2000
Tellurium	2440	250	50	1500

Graphite cores, side arms and powder were baked under vacuum for 6 h (18 h for lead) at 1700°C before use. Absorbances were measured on a Perkin-Elmer 300S atomic absorption spectrometer using a bismuth (Pye Unicam Ltd.), lead (Activion Glass Ltd.) or tellurium (S. & J. Juniper Ltd.) hollow-cathode lamp at wavelengths of 306.8, 283.3 and 214.3 nm, respectively. All measurements were made without damping, i.e., with a time constant of 0.2 s. The masses of samples added to the furnace were determined with a 5-place balance.

Calibration graphs

For the determination of bismuth in copper containing 0.01—2.5 $\mu g\ Bi\ g^{-1}$, calibration graphs of peak area (absorbance × seconds) versus mass of bismuth were obtained by dropping increasing masses of copper SSC 3 (10—30 mg, 0.59 $\mu g\ Bi\ g^{-1}$) into the graphite core under conditions capable of producing absorbances up to 0.25. For the dilute copper alloys CA 5 and CA 6 with bismuth contents in excess of 2.5 $\mu g\ g^{-1}$, the calibration graph was prepared in a similar way with alloy CA 7 (2.3 $\mu g\ Bi\ g^{-1}$), which was standardised against SSC 3. No scale expansion was used with alloy CA 7 but × 5 scale expansion with alloy SSC 3. Peak areas were determined by multiplying the peak height (absorbance) by the peak width at half peak height (s).

For the determination of lead in copper specimens containing 0.8—15 $\mu g\ Pb\ g^{-1}$, calibration graphs of peak areas versus mass of lead were obtained by dropping increasing masses of copper SSC 2 (5—20 mg, 6.1 $\mu g\ Pb\ g^{-1}$) into the graphite core. For the analysis of SEN 337-353, a calibration graph of peak height versus mass of lead was prepared using copper STD 1 (0.8 μg $Pb\ g^{-1}$), which was standardised against SSC 2. Scale expansion (× 10) was employed. Peak heights rather than peak areas were used for SEN 337—353 and the calibration graph, because with such a small absorbance for SEN 337—353, it was not possible to measure the areas of the peaks precisely enough.

For the determination of tellurium in copper containing 0.8—5 $\mu g\ Te\ g^{-1}$, calibration graphs of peak area versus mass of tellurium were obtained by dropping increasing masses of copper STD 2 (5—30 mg, 1.65 $\mu g\ Te\ g^{-1}$) into the graphite core. Peak heights rather than peak areas were used for SEN 337—353, SEN 399—416 and the calibration graph, for the same reason as given above for lead.

Procedure for the determination of bismuth, lead and tellurium in coppers

When a series of copper samples is to be analysed, suitable masses are dropped into the graphite core over a period of 2—3 h; during the same run but generally at the start of the run, various masses of SSC 3 or CA 7 (for bismuth), SSC 2 or STD 1 (for lead) or STD 2 (for tellurium) are also added for construction of a calibration graph. Scale expansion is not required when the concentrations of bismuth, lead and tellurium are expected to be in excess of 2.5, 0.8 and 0.5 $\mu g\ g^{-1}$, respectively. A scale expansion of X 5 is used when the concentrations of bismuth and tellurium are expected to lie within the range 0.1—2.5 $\mu g\ g^{-1}$ or be less than 0.5 $\mu g\ g^{-1}$, respectively. A scale expansion of X 10 is used when the concentrations of bismuth and lead are expected to be less than 0.1 and 0.8 $\mu g\ g^{-1}$, respectively. When the run has been completed, the calibration graph is drawn and the average concentrations of bismuth, lead or tellurium in the samples are calculated.

RESULTS AND DISCUSSION

The calibration graphs for bismuth, lead and tellurium were straight lines through the origin whether peak area or peak height was used. From typical graphs the masses of bismuth, lead and tellurium producing 1% absorption were 0.3, 1 and 0.2 ng, respectively. Results for the determination of bismuth, lead and tellurium in a range of copper and low-alloy copper samples are presented in Tables 3, 4 and 5, respectively.

As can be seen from Table 3, the results for bismuth obtained by using the induction furnace are in good agreement with the independent results for samples supplied by CANMET and BICC Metals, but those for samples

TABLE 3

Results for the determination of bismuth in copper

Copper sample[a]	Bi content ($\mu g\ g^{-1}$)		No. of samples	R.s.d. (%)
	Stated	Found		
SSC1	1.15	1.10	6	6
SSC 2	0.10	0.09	11	20
SSC 4	0.23	0.27	6	11
STD 1	0.45	0.41	6	4
STD 2	0.90	0.91	6	5
SEN 337-353	≤0.02	0.015	12	45
SEN 399-416	0.05	0.08	6	12
CA 5	12.5	10.7	6	14
CA 6	6.4	5.9	6	7
CA 7	2.7	2.3	12	4
CA 8	1.4	1.1	12	7

[a]SSC ~~and STD~~ samples supplied by CANMET, SEN samples by BICC, and CA5-8 by Johnson Matthey.

and STD

TABLE 4

Results for the determination of lead in copper

Copper sample	Pb content ($\mu g\ g^{-1}$)		No. of samples	R.s.d. (%)
	Stated	Found		
SSC 3	4.6	4.2	6	4
SSC 4	15.8	14.7	5	5
STD 1	0.8	0.8	6	9
STD 2	2.6	2.7	6	5
SEN 337—353	≤0.1	0.2[a]	10	26
SEN 399—416	0.9	0.8	12	8
CA 5	8	9.3	6	4
CA 6	4.5	5.2	12	8
CA 7	3	3.4	6	7
CA 8	3	3.8	6	8

[a]Peak height used.

CA 5—CA 8 supplied by Johnson Matthey are slightly lower than the stated results. However, CA 5—CA 8 form part of a series of spectrographic standards made and analysed twenty-seven years ago and the bismuth contents given on the certificates must be viewed with caution. The limit of detection for bismuth in copper with the induction furnace, taken as twice the standard deviation of the 12 results for SEN 337—353, was 0.014 $\mu g\ g^{-1}$.

As is evident from Table 4, the present results for lead are in good agreement with the independent results. The limit of detection for lead in copper was calculated to be 0.1 $\mu g\ g^{-1}$ by employing the ten results for lead in SEN 337—353.

The results obtained here for tellurium are in good agreement with the independent results except, at first sight, for copper SSC 2. However, the CANMET result for tellurium in SSC 2 has a standard deviation of 0.51 $\mu g\ g^{-1}$ and our result of 0.8 $\mu g\ g^{-1}$ is within one such standard deviation of the stated content (1.24 $\mu g\ g^{-1}$). Hence the agreement can be considered to be acceptable. The limit of detection for tellurium in copper was calculated to be 0.02 $\mu g\ g^{-1}$ by employing the twelve results for tellurium in SEN 399—416.

In the determination of bismuth, lead and tellurium in copper using the temperatures given in Table 2, a check for background absorption was made by replacing the hollow-cathode lamps with a hydrogen lamp and by dropping milligram samples of copper into the induction furnace. The maximum absorbances recorded were 0, 0.005 and 0.01 for bismuth, lead and tellurium, respectively. These were considered to be negligible and, therefore, no background corrector was used in this work. However, copper boils at 2567°C and the use of a background corrector would be advisable if core temperatures in excess of 2450°C were employed. An attempt was made to determine antimony and selenium in copper at 2450°C but the furnace temperature was obviously too low for a successful determination of these elements.

TABLE 5

Results for the determination of tellurium in copper

Copper sample	Te content ($\mu g\ g^{-1}$)		No. of samples	R.s.d. (%)
	Stated	Found		
SSC 1	4.6	4.9	11	9
SSC 2	1.2	0.8	12	7
SSC 3	2.5	2.5	6	4
SSC 4	1.4	1.2	5	8
STD 1	0.80	0.81	6	13
SEN 337—353	0.07	0.07[a]	6	10
SEN 399—416	0.04	0.04[a]	12	22

[a]Peak height used.

It is possible that antimony could be determined in copper by using the induction furnace, background correction and the maximum furnace temperature of 2640°C but even this temperature is likely to be too low for the determination of selenium. A switch to a resistively-heated furnace such as the Instrumentation Laboratory 555 furnace, which can attain temperatures in excess of 2640°C, might lead to the satisfactory determination of selenium in copper. Selenium can be determined in nickel-base alloys by adding chips to an IL 555 furnace in an atomic absorption spectrometer fitted with a background corrector, using a maximum furnace temperature of 3000°C [26].

Silver is not usually considered to be a detrimental trace element in copper but very low concentrations of silver in copper could be determined with the induction furnace if necessary. A straight-line calibration graph through the origin was obtained for silver when the lowest practicable temperature of 2120°C was used with the 338.3-nm resonance line and 0.5—3 mg samples of copper SSC 2 stated to contain 13.9 μg Ag g^{-1}. The mass of silver producing 1% absorption was 0.1 ng; this corresponds to a limit of detection of about 0.01 $\mu g\ g^{-1}$ for silver in a 10-mg sample of copper. Samples containing 0.01—2 μg Ag g^{-1} could be analysed by using the induction furnace. By employing the more usual 328.1-nm resonance line, which yields absorbances about double those for the 338.3-nm line, and a higher furnace temperature, it should be possible to determine silver in copper with a limit of detection of about 0.003 $\mu g\ g^{-1}$.

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Determination of trace elements in metals by atomic absorption spectrometry with introduction of solid samples into furnaces: an appraisal

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Abstract—The determination of trace elements in metals by atomic absorption spectrophotometry with introduction of solid samples into furnaces has been reviewed from the first paper in 1965 until the present day. The need for this type of analysis is considered along with other analytical techniques that can provide useful information. Early developments up to 1975 are presented and discussed but the main emphasis is on work undertaken during the past five years. Information is provided on homogeneity of samples, methods of calibration, accuracy, precision and limits of detection to show that this technique is the most convenient available for the determination of volatile trace elements in metals at concentrations less than 10 $\mu g\,g^{-1}$.

The Need for the Determination of Trace Elements

Because certain trace elements have detrimental effects on the properties of metals, it is necessary to determine the concentrations of these elements sometimes at levels below 1 $\mu g\,g^{-1}$ to ensure that metals of adequate quality have been produced. With certain steels it has been specified that the contents of bismuth, lead and antimony should not exceed 10, 30 and 10 $\mu g\,g^{-1}$ respectively [1–3]. For the analyst, these levels are not particularly low, but the analytical problem becomes more severe as we move to copper and nickel-base alloys. For example, the annealing behaviour of copper wire is adversely affected by the presence of lead, antimony, bismuth, selenium and tellurium within the concentration range of 0.3 to 10 $\mu g\,g^{-1}$ [4]. For nickel-base alloys, the SAE Aerospace Metal Specification (AMS) 2280 lists the maximum permissible bismuth content as 0.5 $\mu g\,g^{-1}$ [5] and the DIN 1701 Preliminary Standard (1974) stipulates a maximum bismuth concentration of 0.2 $\mu g\,g^{-1}$ for primary nickel [6]. The specification for grade R. 99.95B (BCS 375:1977) states that the concentrations of silver and thallium in refined nickel should not exceed 1 and 0.2 $\mu g\,g^{-1}$ respectively [7]. The accurate determination of such low concentrations of elements is a real challenge to the analytical chemist for ideally the limit of detection of his method should be as low as 0.02 $\mu g\,g^{-1}$ in some cases.

Other Analytical Techniques

The techniques of atomic spectroscopy such as arc/spark emission and atomic absorption spectroscopy with flames have been of great value for trace element determinations but at levels below 10–100 $\mu g\,g^{-1}$, depending on the element to be determined, a pre-concentration procedure is required before applying a spectroscopic finish. For arc/spark emission this can take the form of precipitation of trace elements from a solution of an alloy on to a suitable carrier and, for atomic absorption spectroscopy, pre-concentration by solvent extraction has been widely applied. However many erroneous, high results are to be found in the literature, when this technique has been used, because it was not realized in the earlier days before the widespread use

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Table 1. Boiling points of selected elements occurring in metals [12]

Element	b.p. (°C)	Element	b.p. (°C)
Gallium	2403	Magnesium	1090
Indium	2080	Calcium	1484
Thallium	1457	Aluminium	2467
Tin	2270	Silicon	2355
Lead	1740	Titanium	3287
Arsenic	613 (sub.)	Vanadium	3380
Antimony	1750	Niobium	4742
Bismuth	1560	Chromium	2672
Sulphur	445	Molybdenum	4612
Selenium	685	Tungsten	5660
Tellurium	990	Manganese	1962
Silver	2212	Iron	2750
Cadmium	765	Cobalt	2870
Zinc	907	Nickel	2732
		Copper	2567

of background correctors, that molecular absorption and light scattering with flames could contribute very appreciably to the absorbance signal.

The advent of atomic absorption spectrometry (AAS) with furnaces for analysing solutions of alloys has lowered the limit of detection for trace elements in metals to about 0.1–1 $\mu g\,g^{-1}$, see, for example, references [8–10], but even these limits of detection are not good enough in some cases. Also as the limit of detection gets lower, the problems of blanks from reagents can become more severe, and it would be particularly useful to have methods of analysis applied directly to the metals or alloys themselves without a dissolution step. From this point of view, neutron activation analysis and spark source mass spectrometry are attractive techniques but neither is widely available and the limit of detection of the latter is not so exceptional varying from 0.02 $\mu g\,g^{-1}$ (aluminium) to 2 $\mu g\,g^{-1}$ (iron) for trace elements in nickel-base alloys [7]. Hollow-cathode emission spectroscopy with limits of detection between 0.01 and 10 $\mu g\,g^{-1}$ often has the required sensitivity [11] but there was a need for another solid-sample technique with similar or better limits of detection, if only to check the reliability of the results obtained by hollow-cathode emission spectroscopy.

THE VOLATILITY OF TRACE ELEMENTS

The elements that are undesirable in certain steels and in high-temperature alloys include thallium, tin, lead, arsenic, antimony, bismuth, sulphur, selenium, tellurium, silver, cadmium and zinc. In copper, trace levels of lead, arsenic, antimony, bismuth, sulphur, selenium and tellurium are detrimental. Fortunately the boiling points of all these elements are relatively low and are given in Table 1. Thus is should be possible to volatilize these elements from a graphite furnace into the light path of an atomic absorption spectrometer at furnace temperatures up to 3000°C provided that bonding between the trace element and another element or elements in the molten metal globule is not sufficiently strong to inhibit the release of trace element into the vapour phase. Major elements in steels, high-temperature alloys and copper usually boil at temperatures considerably in excess of these for trace elements (see Table 1). Only manganese and silicon can contribute substantially to the vapour pressure at temperatures below 2400°C.

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Developments Between 1960 and 1975

Graphite furnaces for atomic absorption spectrometry were developed as a result of the pioneering work of L'Vov [13]. Peak shaped recordings of absorbance versus time are obtained after a solid sample is introduced to a furnace. The absorbance increases to a maximum and then decreases as atoms of the trace element volatilize into the light path of the atomic absorption spectrometry and are then removed from the light path by diffusion or by a gentle stream of inert gas flowing through the furnace.

The determination of trace elements in metals by atomic absorption spectroscopy after introducing solid samples to a furnace was first reported by Nikolaev in 1965 [14]. He determined trace amounts of aluminium and zinc in refractory metals by introducing up to 10 mg masses of metal samples in the form of powder or chips into a L'Vov furnace. Calibration was carried out using standard solutions of aluminium and zinc with the measurement of maximum absorbance. The determined aluminium contents varied from 0.17 $\mu g\,g^{-1}$ in niobium to 2 $\mu g\,g^{-1}$ in molybdenum and the zinc content of tungsten was found to be 0.58 $\mu g\,g^{-1}$. Relative standard deviation was 15% for 0.65 $\mu g\,g^{-1}$ of aluminium in tungsten. However, although the method is certainly semi-quantitative, its accuracy is not known definitely because trace element contents by an independent method were not available. Up to 20 determinations per hour could be made.

In 1969 Headridge and Smith started a series of investigations on the determination of trace elements in metals using the addition of solid samples to induction furnaces [15–18]. Firstly results were obtained with a horizontal furnace but its maximum temperature of 1900°C was considered to be too low and a vertical furnace with a maximum temperature of 2500°C was later employed. The results of these early investigations were described in a review lecture [18]. These workers constructed calibration graphs of absorbance vs concentration ($\mu g\,g^{-1}$) by adding 5 mg samples of standard alloys, usually one or two chips, to the furnace under appropriate conditions, or of absorbance vs mass of trace element by adding similar weights of samples to the furnace. These calibration graphs were then used in the analysis of further samples to assess accuracy and precision. Typical data are shown in Tables 2 and 3 [18]. It can be seen that accuracy is good and precision reasonable. As will be seen later, relative standard deviations of 5–15% have been obtained by many workers for the analysis of solid samples. In the work of Headridge *et al.* the peak height of the transient

Table 2. Experimental conditions and masses and concentrations for 1% absorption

Determination	Line (nm)	Temperature (°C)	Mass (ng)	Concentration for 5 mg sample ($\mu g\,g^{-1}$)
Cd in Zn	228.8	1050	0.4	0.08
Bi in Fe	306.8	1775	1.4	0.3
Bi in cast iron	306.8	2400	2.0	0.4
Zn in Al–Si	307.6*	2350	60	12
Al in mild steel	309.3	2450	25	5
Sb in mild steel	231.1	2400	4	0.8
Sn in steel	284.0	2400	50	10

*The less sensitive resonance line at 307.6 nm was used.

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Table 3. Accuracy and precision of the analyses

Determination	Number of samples analysed	Relative standard deviation (%)	Content by this method (%)	Content by independent method (%)
Cd in Zn	6	4	0.0013	0.0013
Bi in Pb	10	8	0.0043	0.0040
Bi in cast iron	10	8	0.0066	0.0063
*Zn in Al–Si	8	4	0.148	0.15
Al in mild steel	10	7	0.046	0.048
Sb in mild steel	8	7	0.017	0.018
Sn in steel	7	8	0.032	0.030

* The less sensitive line at 307.6 nm was used in this determination.

absorbance signal was measured. Calibration graphs were curved towards the mass axis partly because of the sluggish response of the amplification system of the Unicam SP90 atomic absorption spectrometer to a rapidly changing signal. When the time constant of the amplifier was reduced to 0.1 s, curvature of a calibration graph for bismuth in cast iron was reduced and sensitivity improved as expected.

Results of other investigations in these earlier years using solid metal samples added to furnaces were reported by LANGMYHR and coworkers, ISHIBASHI *et al.* and NORVAL *et al.* Using the induction furnace of LANGMYHR and THOMASSEN [19], lead and cadmium were determined in ferromanganese and ferrosilicon after grinding the material to pass a 300-mesh sieve [20]. The solid standard for lead was the ferrosilicon BCS 305, analysed to contain 7.6 $\mu g\,g^{-1}$ of lead by solution AAS in the furnace. Cadmium in solid samples was determined against standard cadmium solutions. One to 25 mg samples were used with final atomization temperatures of 1270 and 1200°C for lead and cadmium respectively. The accuracy of these results cannot be fully assessed because there are no independent data for the materials analysed. However the method was certainly sensitive for cadmium with the cadmium contents for the ferroalloys ranging from 0.002 to 0.01 $\mu g\,g^{-1}$.

LANGMYHR and RASMUSSEN [21] also determined gallium in an analysed sample of aluminium by adding small drillings of aluminium to their induction furnace. The bauxite sample SRM 69A (115 $\mu g\,g^{-1}$ of gallium) was used as a standard. The gallium in the aluminium was determined as 188 $\mu g\,g^{-1}$ compared with an independent value of 170 $\mu g\,g^{-1}$. Atomization temperature was 1900°C, relative standard deviation was 9% and the limit of detection for gallium was about 0.25 $\mu g\,g^{-1}$.

ISHIBASHI *et al.* [22] have determined trace levels of copper, chromium, iron, silicon, manganese and nickel in tantalum powder by adding solid samples to a heated graphite atomizer and employing atomic absorption spectroscopy. Determinations were made at 2000°C. Accuracy was good as compared with results obtained colorimetrically at levels of from 4 to 30 $\mu g\,g^{-1}$ for copper, chromium, iron, silicon and nickel. Copper and manganese contents of 0.15 and 0.05 $\mu g\,g^{-1}$ respectively are reported for a sample of tantalum powder. Incidentally those wishing to determine trace elements in refractory metals using this technique should refer to the paper by NIKOLAEV on estimates of the sensitivity of the atomic absorption analysis of refractory metals [23].

NORVAL and GRIES [24] have determined 2–35 $\mu g\,g^{-1}$ of thallium in metallic cadmium by adding 1.2 mg samples of material to a resistively heated graphite furnace at

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room temperature, ramping the temperature and measuring peak areas with background correction. Specially prepared solid standards were employed. The accuracy of the method was good and the relative standard deviation was below 5%. The limit of detection was about 0.4 $\mu g\,g^{-1}$.

Developments in Recent Years

All these earlier results reported before 1977 were encouraging. With a fast response amplifier and recorder, limits of detection were very low (0.001–10 $\mu g\,g^{-1}$) and the method appeared to have good accuracy at concentrations between 10 and 500 $\mu g\,g^{-1}$ but the apparent usefulness of the method for determining trace elements at concentrations below 10 $\mu g\,g^{-1}$, where it would be most useful, had still to be proved for a range of elements and part of the reason for slow progress towards establishing the real worth of this analytical method lay in the absence of reliable standards for trace elements at concentrations below 10 $\mu g\,g^{-1}$. However by 1975, analytical methods for trace elements had been improved on all fronts, and alloys whose trace element concentrations were known with greater certainty were becoming available. These were often company standards which had been analysed by a number of different techniques such as differential pulse polarography, anodic stripping voltammetry, flame AAS with background correction after solvent extraction, AAS following hydride generation and furnace AAS with solutions after a detailed investigation of interference effects.

As a result of improvements in furnaces and AA spectrophotometers, and the availability of appropriate standards, papers now began to appear in which the real potential of the technique of adding solid metal samples to furnaces was realised for the determination of deleterious trace elements at concentrations below 10 $\mu g\,g^{-1}$.

The principal investigators in recent years have been Marks *et al.* [25], Headridge and coworkers [26–31], Lundberg and Frech [32, 33], and Bäckman and Karlsson [34]. The furnaces used by these workers, the range of elements investigated in some detail and the range of sample masses employed are shown in Table 4.

Table 4. Furnaces employed in the direct analysis of metal samples and types of analysis undertaken

Investigator	Furnace	Analyses reported	Mass range of samples (mg)	Reference
Marks *et al.*	HGA 2100	Pb, Bi, Se, Te, Tl and Sn in Ni-base alloys	1 ± 0.5	[25]
Headridge *et al.*	Induction (laboratory built)	Bi, Pb, Ag and Sb in irons and steels	0.5–20	[26–28, 30]
	(laboratory built)	Bi, Tl, Ag and Te in nickel-base alloys	1–40	[29, 31, 35]
	(laboratory built)	Bi and Te in copper	1–40	[36]
Lundberg *et al.*	CRA 90	Pb in steels and Ni-base alloys	1–5	[32]
	CRA 90	Ag, Bi, Cd and Zn in steels	1–5	[33]
Bäckman *et al.*	IL 455	Pb, Bi, Zn, Ag and Sb in steels and Ni-base alloys	1–22	[34]

[25] J. Y. Marks, G. G. Welcher and R. J. Spellman, *Appl. Spectry.* **31,** 9 (1977).
[26] D. G. Andrews and J. B. Headridge, *Analyst* **102,** 436 (1977).
[27] A. M. Aziz-Alrahman and J. B. Headridge, *Talanta* **25,** 413 (1978).
[28] D. G. Andrews, A. M. Aziz-Alrahman and J. B. Headridge, *Analyst* **103,** 909 (1978).
[29] J. B. Headridge and R. Thompson, *Anal. Chim. Acta* **102,** 33 (1978).
[30] A. M. Aziz-Alrahman and J. B. Headridge, *Analyst* **104,** 944 (1979).
[31] A. A. Baker, J. B. Headridge and R. A. Nicholson, *Anal. Chim. Acta* **113,** 47 (1980).
[32] E. Lundberg and W. Frech, *Anal. Chim. Acta* **104,** 75 (1979).
[33] E. Lundberg and W. Frech, *Anal. Chim. Acta* **108,** 75 (1979).
[34] S. Bäckman and R. W. Karlsson, *Analyst* **104,** 1017 (1979).
[35] J. B. Headridge and R. A. Nicholson, unpublished results.
[36] A. A. Baker and J. B. Headridge, unpublished results.

HOMOGENEITY OF SAMPLES

This method of analysis has been criticised on a number of occasions because it was felt that the concentrations of trace elements determined in samples of such low mass would not be representative of the concentrations in the bulk material. LUNDBERG and FRECH [37] have made a significant contribution to allaying these fears. They analysed decreasing masses of metals for trace concentrations of lead and antimony using furnace AAS after dissolution, to ascertain if the effects of inhomogeneity make an appreciable contribution to the precision of the method. The results are shown in Table 5. If considerable inhomogeneity is present, then the precision of the determinations should increase significantly as sample mass is decreased. There is evidence that some inhomogeneity in the distribution of lead and antimony in the mild steel and of lead in the ferromolybdenum is present, but this is not significant even for the 2 mg masses. Therefore it can be concluded that lack of homogeneity will not contribute in an unacceptable manner to the overall precision of a determination when solid samples of metals are analysed directly by furnace atomization and atomic absorption spectroscopy. Also a result, which is the average of, say, six determinations of a trace element in 2–50 mg samples of metal chips, will be an accurate determination of the concentration of that element in the bulk material.

METHODS OF CALIBRATION

BÄCKMAN *et al.* [34] and MARKS *et al.* [25] employed calibration graphs of absorbance vs concentration, while HEADRIDGE and coworkers [26–31] used calibration graphs of absorbance vs mass of trace element. MARKS and HEADRIDGE except in the most recent investigations, used peak heights (maximum absorbance) for calibration graphs while BÄCKMAN employed peak areas (integrated absorbance). LUNDBERG [32, 33] preferred to make a direct comparison of normalised peak areas for a standard and a sample for analysis when calculating results.

BÄCKMAN and KARLSSON [34] stated that integrated absorbance is a linear function of the absolute amount of the element measured and is independent of the mass of the sample. LUNDBERG and FRECH [32] reported that more precise and more accurate results for the determination of lead in alloys are obtained using peak area rather than peak height measurements, and that adding samples to a constant temperature cup (isothermal heating) yields more accurate results than those obtained by adding samples to the furnace at ambient temperature and ramping the temperature until atomization has occurred (non-isothermal heating). HEADRIDGE and coworkers employed isothermal heating in all their investigations. Undoubtedly the best conditions are isothermal heating coupled with area measurements but results of good accuracy have been obtained for many alloys, as will be reported later, when peak area measurements in

Table 5. Variation of relative standard deviation with sample mass

	Relative standard deviation (%)				
Sample mass (mg)	Pb in BCS 335	Pb in BCS 330	Sb in BCS 330	Pb in JK 16A	Pb in SANICRO 72
100	2.7				
50	2.5	1.6			
25	4.8	5.5	2.5	3.8	3.3
10	2.7	6.3	3.7	7.2	4.8
5	3.3	7.0	6.1	5.4	3.5
2	4.1	7.0	6.4	9.0	

The alloys are as follows: BCS 335—austenitic stainless steel; BCS 330—mild steel; JK 16A—ferromolybedenum; SANICRO 72—nickel-base alloy.

[37] E. LUNDBERG and W. FRECH, *Anal. Chim. Acta* **104**, 67 (1979).

conjunction with non-isothermal heating (BÄCKMAN) or peak height measurements with isothermal heating (HEADRIDGE) have been used. Peak height measurements coupled with non-isothermal heating have also yielded results of acceptable accuracy (MARKS).

However peak height measurements can lead to erroneous results under certain circumstances. For example, BAKER and HEADRIDGE [36] determined the tellurium content of the standard copper SSC 1 as 6.8 $\mu g\,g^{-1}$ using peak height measurements with BICC 2 containing 1.65 $\mu g\,g^{-1}$ of tellurium as a standard. The certified tellurium content of SSC 1 is 4.6 $\mu g\,g^{-1}$. When peak area measurement was employed for both SSC 1 and the calibration graph, the tellurium content of SSC 1 was found to be 4.9 $\mu g\,g^{-1}$, which is a much more accurate result. Therefore peak area measurements (integrated absorbances) are strongly recommended when analysing solid metal samples.

BÄCKMAN *et al.* [34] found that even with area measurement, the integrated absorbances for standard solutions of an element were approximately 10% greater than the integrated absorbances for identical masses of the element volatilized directly from the metal matrix. Therefore calibration using the direct addition to the furnace of metallic chips of a standard alloy or alloys is recommended. It would be of considerable interest to see if standard solutions of nitrates, dispensed on to thin graphite discs, could be employed with isothermal heating and peak area measurements as a means of producing calibration graphs for the analysis of solid metal samples. However this does not yet seem to have been investigated.

LUNDBERG and FRECH [33] describe an autosampler for adding solids to a Varian CRA 90 graphite cup either at ambient temperatures for non-isothermal heating or at a constant high temperature (isothermal heating). Generally blank firing signals obtained with the use of hollow cathode lamps were low (0.00–0.03 A.s) and accurate determinations were possible without using a background corrector. HEADRIDGE and coworkers operate their instrument without background correction and have frequently checked for any absorbance caused by scattering or by molecular species in their induction furnaces but, so far, absorbance of this type has always been absent or negligible up to 2640°C, the maximum temperature attainable with their latest induction furnaces.

ACCURACY, PRECISION AND LIMITS OF DETECTION

Both BÄCKMAN [34] and HEADRIDGE [26] have stated that large varying amounts of manganese vapour did not affect the accuracy of the determination of trace elements in steel. As a result of extensive studies, BÄCKMAN has concluded that wide variation in the concentration of the main elements of the matrix have little or no effect on the results of the analysis.

Data on precision and limits of detection are presented in Table 6. It can be seen that the average relative standard deviations of these methods usually lie between 5 and 10%. This precision would not be acceptable for the determination of major elements but at trace levels it is satisfactory. The method of analysis is fairly fast with a fresh sample being added to a furnace every 2–3 min. This means that by averaging the results for, say, six samples a result of good accuracy is achieved. On the whole the limits of detection are excellent with the majority lying well below 0.1 $\mu g\,g^{-1}$.

The graphite boats used by BÄCKMAN *et al.* [34] in the IL 455 furnace can only accommodate a small number of samples. For silver and lead, four duplicate determinations were carried out with one boat. For bismuth and zinc, this could be increased to nine duplicate determinations. The graphite boat was changed for each re-calibration which consisted of adding a standard to check and correct for sensitivity changes. However with antimony a new boat was required for each determination.

The Varian CRA 90 cup used by LUNDBERG and FRECH [32, 33] can be used for a maximum of 40 firings. The graphite core of the induction furnace of HEADRIDGE *et al.* [26] can be employed for the analysis of 500 samples before replacement, provided that there is no premature failure of the silica sheath around the core.

Table 6. Data on precision and limits of detection

Determination	Average relative standard deviation (%)*	Limit of detection ($\mu g\,g^{-1}$)	Reference
Pb in irons, steels and Ni-based alloys	10	0.02	[34]
	9	0.02	[25]
	7	<0.06	[32]
	7	<0.05	[28]
Bi in irons, steels, Ni-base alloys and copper	6	0.03	[34]
	7	0.02	[25]
	8	0.05	[33]
	6	0.004 (steels)	[26]
	10	0.02 (Ni-base)	[29]
	8	0.02 (Cu)	[36]
Ag in irons, steels and Ni-base alloys	5	0.01	[34]
	7	<0.03	[33]
	7	0.005 (steel)	[27]
	11	0.014 (Ni-base)	[31]
Sb in irons, steels and Ni-base alloys	6	5†	[34]
	12	0.12	[30]
Zn in steels and Ni-base alloys	5	1‡	[34]
	13	10‡	[33]
Tl in Ni-base alloys	9	0.03	[25]
	6	0.004	[31]
Te in copper and Ni-base alloys	17	0.06 (Ni-base)	[25]
	8	0.008 (Cu)	[36]
Cd in steels and Ni-base alloys	12	0.01	[33]
Se in Ni-base alloys	17	0.2	[25]
Sn in Ni-base alloys	25	0.3	[25]

* For concentrations in excess of 0.1 $\mu g\,g^{-1}$.
† Using a less sensitive line at 259.8 nm.
‡ Using the less sensitive line at 307.6 nm.

To illustrate the accuracy of these methods, a selection of results from the publication of BÄCKMAN [34], LUNDBERG [32, 33] and HEADRIDGE [26, 28, 29] are shown in Tables 7 and 8. It can be seen that the results obtained by different workers are in good agreement and prove that the methods where solid samples are added to furnaces are indeed accurate.

Table 7. Data for the determination of lead in irons, steels and Ni-base alloys

Alloy	Lead content ($\mu g\,g^{-1}$) determined by			Comparative value ($\mu g\,g^{-1}$)
	BÄCKMAN	LUNDBERG	HEADRIDGE	
BCS 331	5.4		5.9	5.3
333	6.0		6.5	5.8
334	11.3	12	11	11*
335	15.3	15	13	15*
336	7.4	6	6.9	7*
JK 1C		0.2	0.24	<0.5
2C			4.2	4.2*
8C		1.9		2*
SRM 361	0.24		0.27	0.25*
362			3.8	4.3*
363			19	22*
365			0.15	0.15*
BCO 35H	7			7.4
40H	25			25

* From the certificate for the standard alloy.

Table 8. Data for the determination of bismuth in steels and Ni-base alloys

Alloy	Bismuth content ($\mu g\,g^{-1}$) determined by			Comparative value ($\mu g\,g^{-1}$)
	BÄCKMAN	LUNDBERG	HEADRIDGE	
BCS 320	0.52		0.55	
325	0.37		0.35	
334	0.06	0.1	0.047	
335	0.06	0.1	0.062	
336	3.3	3.4	3.4	3.2
JK 8F	0.47	0.5		
SRM 361	4.8			4
363	5.2			6.4
RRF 1			0.61	0.5
2			1.9	1.9

CONCLUDING REMARKS

These methods with solid samples have been shown to be accurate and to have satisfactory precision. The sample is not dissolved and the time of an analysis is only a few minutes. The only pretreatment required is to degrease the chips with a suitable, volatile organic solvent. Because sample masses are small, the chips are weighed on a 5-place balance to the nearest 0.01 mg and an automatic balance saves time.

The method is very sensitive, frequently too much so. Sensitivity can be reduced in certain circumstances by selecting a less sensitive atomic absorption line. Lowering the temperature of the furnace also reduces the sensitivity particularly with isothermal heating but this approach must be used with caution because the volatile trace element can be produced too slowly at lower temperatures and very broad absorbance peaks then result. Sensitivity can also be reduced by damping the output from the amplifier of the atomic absorption spectrometer. However this leads to curved calibration graphs especially when peak heights are measured and should be used only as a last resort.

The technique is suitable for the determination of many trace elements that are sufficiently volatile at 2600°C or lower temperatures. These elements include gallium, indium, thallium, tin, lead, antimony, bismuth, selenium, tellurium, silver, zinc and cadmium. Fortunately many of the elements that are troublesome at very low concentrations in metals are among those listed.

In theory the method should also be suitable for the determination of trace concentrations of magnesium, calcium, aluminium, manganese and copper in metals. However the method is so sensitive for these relatively common elements that appreciable background absorption from these elements can be expected with some furnaces. AZIZ-ALRAHMAN and HEADRIDGE [30] were unable to obtain suitable calibration graphs for very low masses of these elements because of a high background even when using a core made from USP grade graphite and vacuum degassed at high temperature.

At the present time a drawback to using this method is a lack of good standard alloys for calibration purposes but the situation has improved greatly in the last few years. It would be particularly useful if it could be shown conclusively that a procedure had been developed for using standard aqueous solutions of the elements for calibration.

Section 4. Chemical phase analysis with emphasis on the quantitative determination of the types of nitrogen in steel

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The Determination of Mobile Nitrogen in Steel Using an Ammonium Ion-selective Electrode

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An absorption cell containing an ammonium ion-selective electrode has been constructed and used for the determination of mobile nitrogen in steel: this nitrogen is released as ammonia when the steel is heated at 500 °C in a stream of hydrogen. The cell was used in conjunction with a digital voltmeter and a recorder in order to obtain a continuous record of the progress of the reaction between mobile nitrogen and hydrogen. Results are presented for the determination of 0·0005–0·0108 per cent. of mobile nitrogen in 10 steels using the new equipment and are compared with those obtained by using a spectrophotometric finish based on indophenol blue. The method, with relative standard deviations of 0·0001–0·0003 per cent., is more precise than that with the spectrophotometric finish, with relative standard deviations of 0·0002–0·0006 per cent.

The mechanical properties of steel are greatly affected by the content of nitrogen, which is usually present within the range 0·001 to 0·05 per cent. Its presence can be harmful, causing age-hardening and flaws in pressings, and the presence of aluminium nitride can result in inter-granular fracture. The presence of nitrogen can also be beneficial by improving the strength and creep properties of steels.[1] Usually nitrogen occurs in steels both as mobile nitrogen and as stable nitrides of elements such as aluminium, silicon, titanium, zirconium, vanadium, niobium and chromium; the nitrogen in stable nitrides is referred to as combined nitrogen. The mobile nitrogen is less strongly bound in steel, occurring as atomic nitrogen or as less stable nitrides of iron and manganese. The ratio of mobile to combined nitrogen, and thus the properties of a steel, can be changed by heat treatment. Hence, for the control of heat treatments, a knowledge of the mobile and combined nitrogen contents is most helpful.

The total nitrogen content of a steel can be determined by use of a Kjeldahl method, in which the nitrogen is converted into ammonia and determined by a suitable titrimetric or colorimetric procedure. The combined nitrogen content of a steel can be determined by using a similar procedure after separation of stable nitrides and other compounds from the steel, following dissolution of the metals, by using a methyl acetate - bromine mixture. The difference between the total and combined nitrogen values is the mobile nitrogen. However, a more convenient way to determine mobile nitrogen is to pass hydrogen over steel millings at 500 °C. The mobile nitrogen is thus converted into ammonia, which is absorbed in a suitable solution and determined spectrophotometrically as indophenol blue.[2–4] The success of this thermal method depends on two factors. Firstly, there must be no reaction at 500 °C between the mobile nitrogen and a metal in the steel, which will result in the precipitation of more stable nitride. Such a reaction would lead to a low result for mobile nitrogen. It has been established that such a reaction does not occur between mobile nitrogen and aluminium, silicon or titanium at 500 °C, hence, such an interfering reaction will not occur with most commercial steels. The interfering reaction occurs only with certain special steels, which contain appreciable concentrations of elemental vanadium and niobium.[2] Secondly, it is important that no stable nitrides should dissociate at 500 °C as this would give rise to high results for mobile nitrogen. It appears that this is an interfering effect only for steels that contain appreciable concentrations of chromium nitride,[2] and carbon and low-alloy steels of this type are rarely produced. Therefore, it is generally agreed that the thermal method, using hydrogen at 500 °C, is reliable for the determination of mobile nitrogen in most commercial carbon and low-alloy steels. Actually, the optimum temperature for this extraction method for mobile nitrogen may not be 500° C for all types of steels, but this information can be acquired only by more extensive use of the technique.

The thermal method using hydrogen, coupled with an indophenol blue spectrophotometric finish, has been used successfully in our laboratory for some time. However, a spectro-

photometric determination of the ammonia that is evolved has the disadvantage that one cannot be certain that all of the mobile nitrogen from a particular alloy sample has been converted into ammonia at 500 °C within a particular period of time, unless multiple runs with increasing collection times are undertaken. The collection time for ammonia depends on the flow-rate of the hydrogen and on the dimensions of the steel millings. Millings that have at least one dimension less than 0·5 mm are usually used; also, collection times of the order of 1 h are often used.

Clearly, it would be advantageous to have available a simple method for continuously recording the amount of mobile nitrogen that has been extracted as ammonia during a run and to know beyond doubt when all of the mobile nitrogen has been extracted. Such a method is described in this paper. To this end a special absorption cell for ammonia, incorporating an ammonium ion-selective electrode in a triethanolamine - triethanolammonium ion buffer solution, has been constructed. The potential difference between this electrode and a mercury - mercury(I) sulphate reference electrode is passed to a digital voltmeter and continuously recorded on a potentiometric recorder. The point at which all of the mobile nitrogen has been collected can be seen at a glance and the mobile nitrogen content of the steel can then be determined immediately by reference to a suitable calibration graph.

Because it was also our intention to compare the quality of the ion-selective electrode results for mobile nitrogen with those obtained by use of colorimetry, the 10 steel samples analysed by the proposed method were first analysed by using the spectrophotometric indophenol blue method.[2–4] In order to obtain useful values for the precision of the methods, six samples of each steel were analysed by use of each method.

Experimental

Apparatus

The apparatus for the release from a 1-g sample of steel of mobile nitrogen as ammonia and its collection and determination was straightforward in design and is shown in Fig. 1.

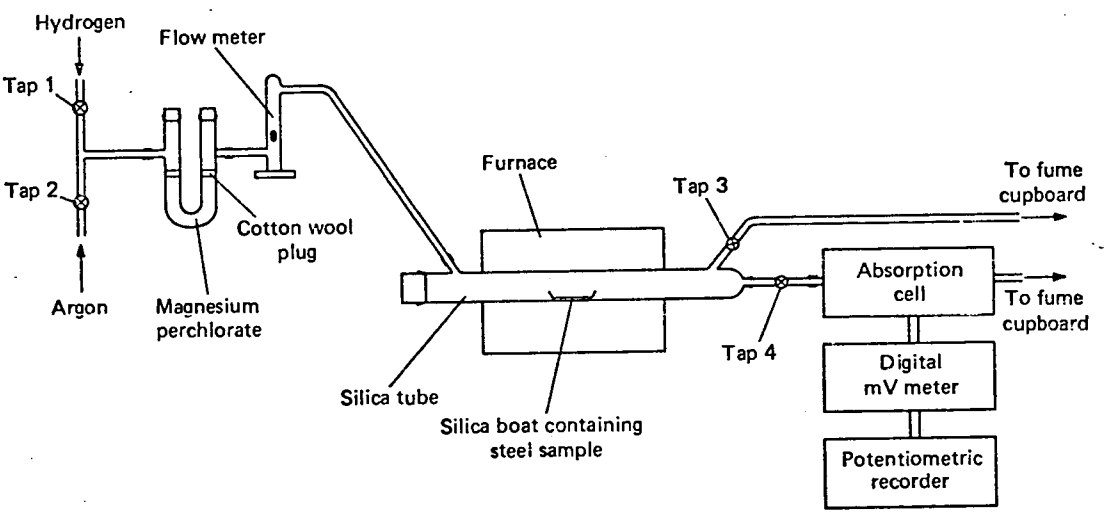

Fig. 1. Apparatus for the determination of mobile nitrogen in steel.

The various components were as follows.

Flow meter. This was a Meterate, Type RS2, fitted with a hydrogen tube (Glass Precision Engineering Ltd., Hemel Hempstead).

Resistance heated tube furnace (maximum temperature 1000 °C). This was made by the Amalgams Co. Ltd., Sheffield, and controlled by a Pye Ether Mini temperature controller. The furnace contained a silica tube of 40 mm internal diameter with a hot zone approximately 150 mm in length.

Silica boats. These boats had internal dimensions of 100 × 17 × 7 mm and were formed from silica sheet 2·5 mm thick.

Absorption cell. This contained a mercury - mercury(I) sulphate reference electrode (see Fig. 2).

Ammonium - potassium ion-selective electrode. EIL, Model 1057 200.

Digital millivoltmeter. EIL, Model 7060.

Potentiometric recorder. Oxford, 3000 series, single pen.

Constant-temperature bath, thermostatically controlled at 25 °C. For immersion of the absorption cell.

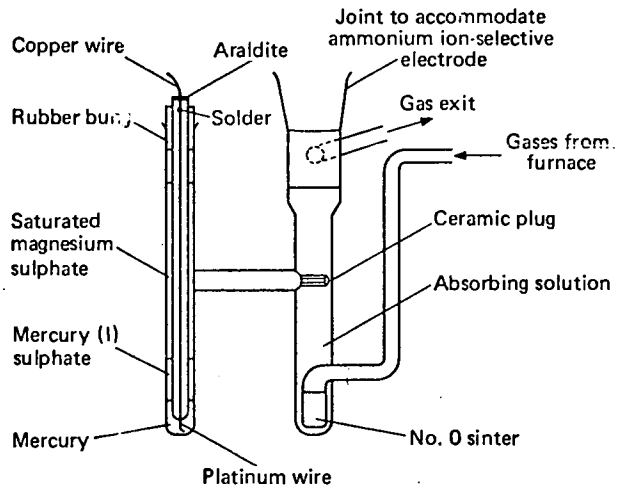

Fig. 2. Absorption cell for the ammonia produced by reaction of hydrogen with mobile nitrogen from a steel sample.

Reagents

Acetone. Redistilled analytical-reagent grade.

Hydrogen. Air Products Ltd., high-purity grade, 99·99 per cent.

Argon. Air Products Ltd., ultra-high-purity grade, 99·999 per cent.

Triethanolamine. Fisons SLR grade.

Hydrochloric acid, 1·000 M. This was prepared from ConvoL solution, Hopkin and Williams Ltd.

Ammonium ion free water. This was prepared by passing distilled water through a column of Amberlite IR-120 ion-exchange resin (H^+ form) and was used throughout this work.

Magnesium perchlorate. Fisons LR grade.

Ammonium chloride solution A. Dissolve 3·821 g of analytical reagent grade ammonium chloride (dried at 140 °C) in ammonium ion free water and dilute to 1 l in a calibrated flask with the same solvent.

1 ml of solution ≡ 1 mg of nitrogen.

Ammonium chloride solution B. Dilute 10 ml of solution A to 100 ml with ammonium ion free water.

1 ml of solution ≡ 100 μg of nitrogen.

Ammonium chloride solution C. Dilute 10 ml of solution B to 100 ml with ammonium ion free water.

1 ml of solution ≡ 10 μg of nitrogen.

Solution for the Absorption of Ammonia

To respond to the ammonium ion-selective electrode the ammonia must be fixed as ammonium ion. Triethanolamine and its conjugate acid form a suitable buffer solution for the absorption of ammonia because the pK_a value for triethanolammonium ion at 25 °C is 7·76. In theory, a buffer solution of triethanolamine and triethanolammonium ion in a concentration ratio of 1:10 should have a pH of 6·76 and in such a solution the ratio of

ammonium ion to ammonia resulting from the absorption of ammonia should be 309:1, indicating that the fixing of ammonia as ammonium ion is virtually complete.

Commercial triethanolamine contains some diethanolamine and it was therefore necessary to determine the mass of triethanolamine that was equivalent to 1 mol of hydrogen ion. This was determined by titrating potentiometrically a suitable mass of the triethanolamine with 0·1000 M hydrochloric acid. One mole of hydrogen ion was found to be equivalent to 147·7 g of the commercial base.

Preparation of the buffer solution

One litre of 1 M hydrochloric acid was added, with agitation, to 162·5 g of commercial triethanolamine (1·1 mol) dissolved in approximately 800 ml of water. The solution was then diluted to 2 l. The pH of this BH^+ - B buffer solution (10 + 1) was measured as 6·88 at 25 °C.

Construction of a Suitable Calibration Graph

A graph of cell potential *versus* the logarithm of the concentration of ammonium ion took the form of a straight line down to 10^{-4} M with a slope of 54 mV per unit of $\log[NH_4^+]$. At lower concentrations the line curved increasingly towards the log concentration axis, but the electrode responded satisfactorily to changes in ammonium-ion concentration down to 7×10^{-6} M, which is the concentration of ammonium ion produced when the ammonia equivalent to 0·0001 per cent. of mobile nitrogen in 1 g of steel is absorbed in 10 ml of buffer solution.

A calibration graph of cell potential *versus* concentration of nitrogen as ammonium ion (0·5–8 μg ml^{-1} of nitrogen) was constructed after measuring the potential of the ion-selective electrode *versus* the reference electrode for seven solutions of ammonium ion in the buffer solution; these solutions were prepared as follows. To 50 ml of buffer solution in each of seven 100-ml calibrated flasks add, in turn, 5 ml of ammonium chloride solution C, and 1, 2, 3, 4, 6 and 8 ml of ammonium chloride solution B and dilute each solution with ammonium ion free water to 100 ml.

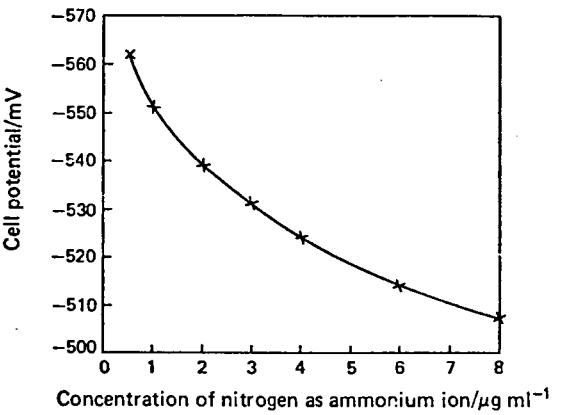

Fig. 3. A typical calibration graph for the determination of nitrogen as ammonium ion collected from steel samples.

The ammonium ion-selective electrode was conditioned before use by standing it in the most dilute calibration solution (0·5 μg ml^{-1} of nitrogen) for 2 d. The solutions were placed in the absorption cell in turn, in order from the most dilute to the most concentrated, and the cell potential was measured with each solution. Several minutes were allowed for the electrode to attain a steady potential, the electrode being agitated during this time. The electrode was washed only with the next solution between readings and not with distilled water. A typical calibration graph is shown in Fig. 3; calibration was carried out every 72 h. The changes in potential of the ammonium ion-selective electrode, when used with the cali-

bration solutions, from one calibration to the next were never in excess of and usually less than 2 mV. When not in use the electrode was stored in the most dilute calibration solution.

Method for the Determination of Mobile Nitrogen in Steel Using the Ion-selective Electrode

With argon flowing through the furnace and the by-pass tube at a rate of 300 ml min^{-1}, turn on the furnace and allow the temperature to become steady at 500 °C. Wash the absorption compartment of the cell with water, followed by acetone, these solvents being removed by means of a hypodermic needle connected to a suction pump. Close tap 3 and open tap 4 so that hot argon passes through the sinter and completely dries the absorption compartment (Note 1). Then close tap 4 and open tap 3 so that the argon by-passes the cell.

Increase the flow-rate of argon to approximately 1·5 l min^{-1} and remove the rubber bung at the end of the silica tube. Place the silica boat containing exactly 1 g of steel into the cool end of the furnace tube nearest the flow meter and replace the bung. Next, purge the furnace tube with argon for approximately 3 min (Notes 2 and 3). Reduce the flow-rate of argon to 300 ml min^{-1} and switch the flow of argon through the absorption cell.

Pipette 10 ml of the buffer solution containing ammonium ion equivalent to 5 μg of nitrogen into the absorption compartment of the cell and insert the ion-selective electrode. Allow the argon to flow through the solution for 5 min and switch the flow of gas to the by-pass tube. Then increase the flow-rate of argon to 1·5 l min^{-1} and push the boat to the centre of the furnace tube. Continue the passage of argon for 2 min and then switch to a stream of hydrogen at a flow-rate of 140 ml min^{-1}. Immediately switch the flow of gas to the absorption cell and continue to pass hydrogen through the cell until the electrode potential has stabilised, showing that no more ammonia is being released from the steel. For most steels this is a period of 120 min. Note the cell potential on the digital voltmeter and read off the concentration of nitrogen in the absorption cell from the calibration graph; then switch back to an argon stream. Determine the blank value for an empty silica boat after passing hydrogen through the apparatus for 120 min.

NOTES—

1. It is important that the inlet arm to the absorption cell should be completely dry while the ammonia is being collected, otherwise some ammonia is absorbed in solution on the sides of the inlet arm before the sinter and low results are obtained.
2. Use steel millings with at least one dimension less than 0·5 mm.
3. For samples containing more than 0·0070 per cent. of mobile nitrogen use 0·5 g of steel.

Calculation of the Concentration of Mobile Nitrogen in the Steel

The passage of hydrogen through the absorption cell for 120 min caused the volume of the solution to diminish from 10·0 to 9·7 ml. The volume change is most easily determined by adding the appropriate buffer solution to the absorption cell from a microburette until the volume is restored to its original value, as shown by a mark on the outside of the cell. During this operation the cell is removed from the bath, tap 4 being open.

For an empty tube:
Initial cell potential $\equiv$ 0·5 μg ml^{-1} of nitrogen = 5 μg of nitrogen for 10 ml of solution
Final cell potential $\equiv x$ μg ml^{-1} of nitrogen = $x \times 9{\cdot}7$ μg of nitrogen for 9·7 ml of solution
Hence, nitrogen as ammonia from the hydrogen (the blank) = $[(x \times 9{\cdot}7) - 5]$ μg

For the steel sample:
Initial cell potential $\equiv$ 5 μg of nitrogen for 10 ml of solution
Final cell potential $\equiv y$ μg ml^{-1} of nitrogen = $y \times 9{\cdot}7$ μg of nitrogen for 9·7 ml of solution
Hence mobile nitrogen from the steel + blank = $[(y \times 9{\cdot}7) - 5]$ μg
Thus mobile nitrogen from the steel = $[(y - x) \times 9{\cdot}7]$ μg

For a 1-g sample the concentration of nitrogen in the steel = $[(y - x) \times 9{\cdot}7] \times 10^{-4}$ per cent.

Method for the Spectrophotometric Determination of Mobile Nitrogen[2–4]

The equipment was identical with that for the ion-selective electrode method except that the ammonia in the stream of hydrogen from the furnace tube was absorbed in 50 ml of 0·001 M hydrochloric acid after passing through a larger No. 0 sinter. A collection time of 70 min was generally employed, with a flow-rate of 220 ml min^{-1}.

Results

Compositions of the Steels

The compositions of the steels analysed by both the spectrophotometric and ion-selective electrode methods are shown in Table I.

TABLE I

COMPOSITIONS OF THE STEELS

	Concentrations of elements in the alloy, per cent.									
Alloy	C	Si	Mn	Ni	Cr	Al	Mo	Ti	Cu	Total N
A	0·31	0·67	0·87	0·04	0·03	0·054	—	—	0·07	0·0108
C	0·30	0·67	0·87	0·04	0·03	0·15	—	—	0·07	0·0092
D	0·29	0·65	0·86	0·04	0·03	0·066	—	—	0·07	0·0122
12N	0·16	0·12	1·17	—	—	—	—	0·024	—	0·0087
13N	0·15	0·17	0·97	—	—	—	—	0·058	—	0·0220
14N	0·15	0·25	1·00	—	—	—	—	0·099	—	0·0228
7	0·33	0·40	1·48	—	—	—	0·33	—	—	0·012
B3275 (A) and (B)	0·28	1·23	0·61	0·04	0·03	—	0·32	—	—	0·012
P74	0·07	1·56	1·11	21·4	15·0	—	0·05	—	—	0·0169

Analysis of the Steels by Using the Ion-selective Electrode Method

Results for the analysis of the steels by this method are shown in Table II and are also compared with the results obtained by the spectrophotometric procedure. The blank corresponded to 0·5 μg or less of nitrogen in 9·7 ml of solution. A typical recording of cell potential *versus* time for a steel is shown in Fig. 4. By using the calibration graph, these cell potentials were converted to concentrations of nitrogen as ammonium ion and a graph of concentration of nitrogen *versus* time is also shown in Fig. 4.

TABLE II

RESULTS FOR THE DETERMINATION OF MOBILE NITROGEN IN STEEL SAMPLES USING THE ION-SELECTIVE ELECTRODE AND A COMPARISON OF THE RESULTS WITH THOSE OBTAINED BY THE SPECTROPHOTOMETRIC PROCEDURE

Steel	Results for the determination of mobile nitrogen using the ion-selective electrode, per cent. × 10⁴*	Average result using the ion-selective electrode, per cent. × 10⁴	Standard deviation using the ion-selective electrode, per cent. × 10⁴	Average result using the spectrophotometric method, per cent. × 10⁴	Standard deviation using the spectrophotometric method, per cent. × 10⁴
A	5·5, 3·5, 6·5, 5·5, 5·5, 6·5	5·5	1	6	2
C	6·5, 9·5, 6·5, 6, 8·5, 8·5	7·5	1·5	9	2
D	4·5, 7·5, 5, 5·5, 6, 6	6	1	6	3
12N	61, 63·5, 63·5, 65·5, 61·5, 65·5	63·5	2	64	7
13N	106, 109, 106, 109, 109, 109	108	1·5	106†	5†
14N	46·5, 44·5, 43, 49, 41, 45	45	3	45	3
7	32·5, 31·5, 31, 30·5, 31, 32·5	31·5	1	28	3
B3275 (A) ‡	7·5, 5·5, 6, 9·5, 9, 8·5	7·5	1·5	8	2
B3275 (B)	31, 31·5, 35·5, 35·5, 36, 37	34·5	2·5	36	6
P74	4, 4·5, 6, 5·5, 5, 6	5	1	7	3

* Collection time 120 min for all samples.
† Ammonia collected for 120 min.
‡ Heat treated and quenched form of B3275 (B).

For most steels the rate of release of ammonia was greatest after the passage of hydrogen for 15 min in the ion-selective electrode method, but ammonia continued to be released at a diminishing rate up to 2 h after switching from argon to hydrogen. A typical graph of the rate of accumulation of nitrogen as ammonium ion *versus* time is shown in Fig. 5.

Discussion

The results shown in Table II are considered to be very satisfactory, excellent agreement between the two methods being achieved. With the spectrophotometric procedure, steel 13N

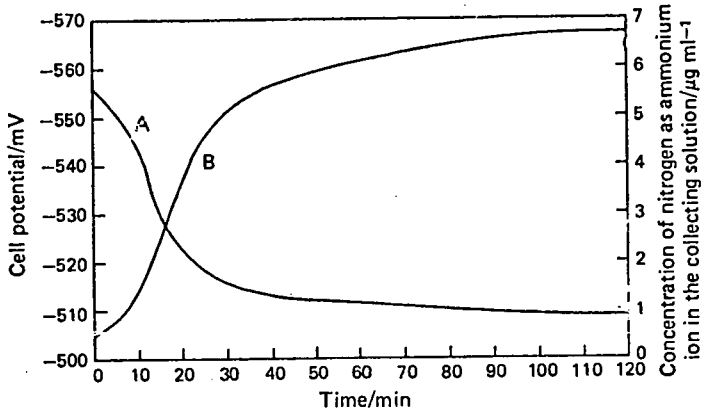

Fig. 4. A, A recording of cell potential *versus* time for steel 12N. B, A graph of nitrogen concentration as ammonium ion in the collecting solution *versus* time for steel 12N.

appeared to contain only 0·0098 per cent. of mobile nitrogen, but this was raised to 0·0106 per cent. when the collection period was increased from 70 to 120 min. This result illustrates the drawbacks of the spectrophotometric procedure with a fixed collection time. Different collection periods arose when using the two procedures because of the different sizes of the No. 0 sinters used in the absorbing solutions. A lower flow-rate inevitably leads to a longer collection period. It is evident from Table II that the precision of the ion-selective electrode method is superior to that of the spectrophotometric method, but its main advantage lies in the fact that the completion of the collection of ammonia for any steel sample is at once obvious to the operator. The use of a potentiometric recorder coupled to a digital voltmeter is not essential but it is a distinct advantage because the amount of ammonia collected is automatically recorded and, while this is occurring, the operator can be engaged in other work.

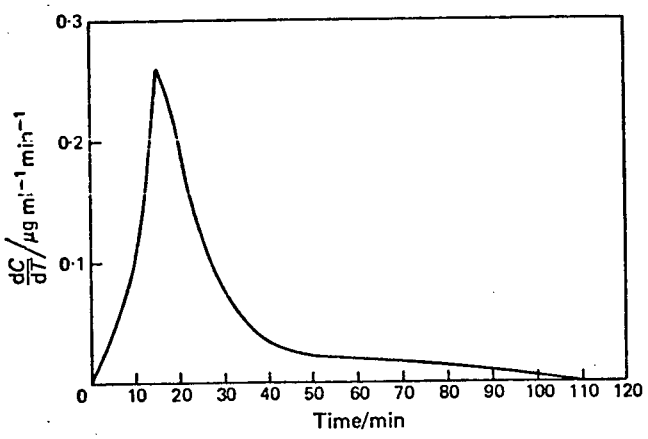

Fig. 5. A graph of the rate of accumulation of nitrogen as ammonium ion in the collecting solution *versus* time for steel 12N. (*C* is the concentration of nitrogen and *T* the time).

The response of the EIL, Model 1057 200, ion-selective electrode to changes in ammonium-ion concentration from more to less concentrated solutions was rather sluggish. The potential of the ion-selective electrode *versus* the reference electrode changed rapidly over a period of a few minutes, and then tended to drift to more negative values very slowly when the electrode was placed in the most dilute standard solution (0·5 μg ml^{-1} of nitrogen) after being in a more concentrated ammonium-ion solution. For the first run on a particular

day the cell potential stabilised quickly at the start of the run because the ion-selective electrode had been standing overnight in the most dilute calibration solution, but for the second and later runs it was inconvenient to wait until the starting potential had stabilised completely before commencing the collection of ammonia. The starting potentials were often 1–2 mV more positive than the corresponding potential on the calibration graph. This was of no consequence as the cell potential that was required for the calculation of mobile nitrogen in a steel was that measured after the passage of hydrogen for 2 h, and a steady potential corresponding to the concentration of ammonium ion in the absorption cell was always achieved under these conditions. It has been suggested that a suitable poly(vinyl chloride) membrane electrode for the ammonium ion would respond more rapidly than the glass membrane electrode to changes in the ammonium-ion concentration, but the EIL 1057 200 glass membrane electrode can be used almost indefinitely and its rate of response is sufficiently rapid for the work described in this study.

All of the steels except P74 were low-alloy steels containing only trace amounts, if any, of vanadium and niobium. Therefore, the results obtained for mobile nitrogen from these nine steels should be reliable. Alloy P74 is a high-alloy steel and might possibly contain some chromium nitride, although silicon forms a more stable nitride than does chromium.[5] However, if the alloy does contain chromium nitride there is little evidence for its breakdown at 500 °C because it can be seen from Table II that its mobile nitrogen content, 0·0005 per cent., is very low, although the total nitrogen content is 0·0169 per cent.

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Short Communication

THE DETERMINATION OF MOBILE NITROGEN IN VANADIUM STEELS BY THE EXTRACTION METHOD WITH HYDROGEN

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Nitrogen is present in steels in the atomic form in solid solution, and combined as nitrides. When hydrogen is passed over fine millings at 500°C, the atomic nitrogen is removed as ammonia [1]. Any iron or manganese nitrides decompose at that temperature and also form ammonia with hydrogen. The nitrogen removed at that temperature is known as mobile nitrogen. The more stable nitrides formed with boron, silicon, aluminium, titanium, zirconium, vanadium, niobium and tantalum are not decomposed in hydrogen at 500°C; this nitrogen is known as combined nitrogen. Certain properties of steel, such as strain aging and toughness are influenced not only by the total nitrogen content, but also by the ratio of mobile to combined nitrogen.

The hydrogen extraction method has not been considered to be reliable for steels containing vanadium or niobium where there is more than 20 ppm of mobile nitrogen [1]. The results obtained for mobile nitrogen in these steels by this method are lower than the differences between the total nitrogen contents by a vacuum fusion method, and the combined nitrogen contents determined after the dissolution of the steels in a bromine—methyl acetate mixture [2]. The iron matrix is dissolved in the bromine—ester mixture, and the atomic nitrogen released, while the stable nitrides remain unattacked. Any iron and manganese nitrides present in the steel are also soluble in the bromine—ester mixture. However, very small particles of stable nitrides may not be retained on the filter, thereby giving a low combined nitrogen result [2].

Fisher and White [1] stated that the mobile nitrogen results for vanadium steels containing more than 20 ppm of mobile nitrogen are low, because of further precipitation of vanadium nitride at 500°C. It was hoped that the apparent mobile nitrogen content of a steel could be increased as the hydrogen extraction temperature was decreased until the mobile nitrogen result was identical with the mobile nitrogen result obtained by the difference method. The effect of the cooling rate of the steel after heat treatment was also investigated, as this is of major importance in considering the mechanical properties of steel.

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TABLE 1

Mobile nitrogen contents of the steels by the hydrogen extraction method at different temperatures
(Duplicate results are given.)

Steel[a]	250°C	350°C	400°C	440°C	500°C	650°C
SG1	<5	86, 80	86, 78	85, 89	66, 63	<5
BSC1	<5	40, 39	42, 38	39, 40	33, 33	<5

[a]The compositions of the steels (%) are:

Steel	C	Si	Mn	S	P	Ni	Cr	Cu	Sn	V
SG1	0.08	0.24	1.51	—	—	—	—	—	—	0.16
BSC1	0.24	0.24	1.45	0.018	0.011	0.046	0.037	0.067	0.009	0.084

SG1 is a vacuum-melted experimental steel, and BSC1 is a commercial cast from British Steel Corporation.

Experimental

The steels SG1 and BSC1 (Table 1) were heated and held at 1100°C and 1150°C, respectively, for 30 min, and then quenched in iced water to obtain a high mobile nitrogen content. Steel SG1 was also cooled at controlled rates between 3.6 and 120°C min^{-1} from 1100°C.

The mobile nitrogen content was determined by the hydrogen extraction method of Headridge and Long [3], at different temperatures between 250°C and 650°C; the collection time (3—5 h) was continued until cessation of ammonia production, which was determined by the ion-selective electrode.

The combined nitrogen content was determined by bromine—methyl acetate dissolution followed by filtration on glass fibre discs, conversion of the insoluble nitrides to ammonium ion by fuming sulphuric acid, followed by steam distillation of ammonia after addition of alkali and spectrophotometric determination of ammonia as indophenol blue [4]. The total nitrogen content was determined by vacuum fusion with a Balzer Exhalograph EN2200.

Results and discussion

Mobile nitrogen determinations. The mobile nitrogen results are shown in Table 1, which also shows the chemical compositions of the steels. The times for the complete extraction of mobile nitrogen were approximately 4.75, 3.5, 3.0 and 3.0 h at 350, 400, 440, 500°C, respectively. The results obtained at 500°C are significantly below those obtained at lower temperatures.

Total and combined nitrogen determinations. The combined nitrogen contents of the steels obtained by the bromine—ester method and the apparent mobile nitrogen contents by difference are shown in Table 2. There is a very large discrepancy between the mobile nitrogen as calculated by difference and the values obtained directly. From Table 1, the results for mobile nitrogen by the extraction method are virtually the same at 350°C, 400°C and 440°C. If precipitation of vanadium nitride were occurring during the extraction of atomic nitrogen, the apparent mobile nitrogen content would be expected to increase as the temperature of extraction decreased. This is noticed only between 500 and 440°C. Hence it appears that the mobile nitrogen results are reliable at the lower temperatures, and that results by the difference method are grossly in error.

At 1100—1150°C, much of the nitrogen in steels SG1 and BSC1 should be in solution [5], and vanadium nitride precipitated during quenching would consist of extremely fine particles, which could have passed through the glass-fibre filters or have been at least partially dissolved in the bromine—ester mixture. There has been some controversy about vanadium nitride recovery in past papers [6, 7].

Very little mobile nitrogen was recovered at 250°C and 650°C (Table 1). A temperature of 250°C is too low for appreciable reaction between atomic nitrogen and hydrogen on a steel surface [8]. Precipitation of vanadium nitride through reaction between atomic nitrogen and elemental vanadium gives a very low mobile nitrogen value at 650°C. In both these steels there is an excess of vanadium over nitrogen on an atomic basis.

Steels SG1 and BSC1 were also heated in argon at 350°C for 1 h before the mobile nitrogen contents of the steels were determined. The results obtained were 80 ppm and 39 ppm, respectively, which is in good agreement with the values of 83 and 40 ppm. Clearly no significant precipitation of vanadium nitride occurred during the heating in argon. These results and those of Table 1 show that the hydrogen extraction method is reliable, if the temperature of extraction is between 350°C and 440°C. The difference method for mobile nitrogen in vanadium steels seems to be seriously in doubt when steels contain very fine particles of this nitride.

Effect of cooling rate on mobile nitrogen values. The mobile nitrogen values as determined by the hydrogen extraction method at 440°C for the steel SG1, cooled at five different rates, are shown in Table 3. The range of equivalent cooling rates from that of air-cooled large section sizes down to water-quenched small sections was investigated; this covers all the

TABLE 2

The distribution of nitrogen (ppm) in the steels

Steel	Total N	Combined N (bromine—ester)	Mobile N (by difference)
SG1	360, 380	65, 68	303
BSC1	160, 170	50, 50	115

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TABLE 3

Effect of cooling rate on mobile nitrogen values

Cooling rate from 1100°C (°C min^{-1})	8,000[a]	120	36	12	3.6
Equivalent cooling of	20-mm bar in water	13-mm bar in air	50-mm bar in air	120-mm bar in air	380-mm bar in air
Mobile nitrogen extracted at 440°C (ppm)	87	12	9	5	<5

[a]Water-quenched.

commercial heat treatment conditions that are likely to be encountered in practice.

In view of the known effects of mobile nitrogen on mechanical properties, these results are very significant. After rapid quenching, 87 ppm of nitrogen are retained in solid solution, whereas at slower cooling rates, the mobile nitrogen content is progressively decreased because of precipitation of vanadium nitride on cooling. At the slowest cooling rate, there is virtually no mobile nitrogen in the steel, which means that all the nitrogen is combined as vanadium nitride. These results also emphasize the ability of vanadium to remove all the nitrogen efficiently from solid solution by controlled heat treatment. Other elements such as aluminium and silicon remove only part of the nitrogen from solid solution under similar heat treatment conditions [9]. However, it must be pointed out that steel SG1 has a much higher total nitrogen content than vanadium steels encountered commercially.

In both steels, the temperatures of 1100 and 1150°C, although sufficiently high for the solution of a significant amount of vanadium nitride, are not high enough to dissolve all the vanadium nitride. However, it is not known how much vanadium nitride precipitates on cooling, even with the rapid cooling rates produced by water quenching. Thus the combined nitrogen values will consist of undissolved vanadium nitride at the solution temperatures (1100 or 1150°C), and vanadium nitride which precipitates on cooling. The variation between 87 and <5 ppm nitrogen in solid solution shows the significance of cooling rate, which has a very important effect on the mechanical properties of steel, such as toughness and creep strength.

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DETERMINATION OF THE TYPES OF NITROGEN IN STEELS CONTAINING ALUMINIUM OR TITANIUM BY AN EXTRACTION METHOD WITH HYDROGEN

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SUMMARY

The extraction method with hydrogen, hitherto used to determine mobile nitrogen in steels over the temperature range 350—450°C, has been employed at higher temperatures to determine nitrogen bound as aluminium nitride, or as titanium nitride or carbonitride. In steels containing only silicon and titanium as deoxidizers, the nitrogen remaining after passage of hydrogen at 600 or 750°C is present as titanium nitride or carbonitride and can be determined by difference. In steels containing only silicon and aluminium as deoxidizers, the nitrogen remaining after passage of hydrogen at 600°C is present as aluminium nitride and can also be determined by difference. This was verified by determining the aluminium nitride indirectly. The nitrogen released from both the aluminium and titanium steels in hydrogen at 600°C probably results from dissociation of submicroscopic particles of manganese silicon nitride.

The presence of nitrogen can have profound effects on the mechanical properties of steels and the determination of total nitrogen in steel has been a requirement for many years. Essentially nitrogen increases the strength and decreases the ductility and toughness of steels. To explain these effects there are many mechanisms which are related to the type of steels and to whether the nitrogen is present as combined nitrogen in nitride precipitates or is in interstitial solid solution in the matrix austenite or ferrite phases. For example, widely dispersed precipitate particles are able to restrict grain coarsening such that fine-grain mild steels or structural steels are produced by controlling, through heat treatment, the precipitation of aluminium nitride, niobium carbonitride, titanium carbonitride and vanadium carbonitride.

The metallurgically soluble nitrogen is referred to as mobile or free nitrogen and can be present interstitially in the iron lattice, in association with substitutional solutes in the iron lattice such as manganese, or in association with dislocations or at grain boundaries. Mobile nitrogen also includes any nitrogen present in discrete nitride phases of the rather unstable iron and manganese nitrides which may possibly be present in some steels [1]. The sum of mobile plus combined nitrogen is the total nitrogen in the steel.

The well known yield phenomena and strain ageing in low carbon steels are

due to the segregation of nitrogen in dislocations. At higher temperatures substitutional—interstitial reactions also produce strengthening by a dislocation locking mechanism. Recently, an important correlation between the impact transition temperature and soluble nitrogen has been discovered in reinforcing steels. The addition of titanium to mild steels in the correct stoichiometric ratio with respect to total nitrogen content to give titanium nitride precipitates, results in a tenfold decrease in mobile nitrogen content associated with a 60°C decrease in the impact transition temperature [2].

These are only a few of the effects of combined nitrogen and mobile nitrogen in steels. By suitable heat treatment or by the addition of certain elements to steels, the ratio of mobile to combined nitrogen can be altered to produce the properties sought by the metallurgist. A knowledge of the concentrations of the various types of nitrogen in steels would be particularly helpful, especially when coupled with information on the distribution of the phase or phases that make up combined nitrogen.

The determination of mobile nitrogen in steels is most conveniently undertaken by passing hydrogen over fine particles of steel at 450°C. At this temperature the mobile nitrogen is removed from the steel as ammonia, which can be determined continuously by using a cell incorporating an ion-selective electrode [3], coulometrically [4] or conductometrically [5]. It has been appreciated for some time that high results for mobile nitrogen could arise if any of the precipitated nitrides dissolved during the passage of hydrogen, and low results would be produced if any further precipitation was to occur in the steel through reaction of a nitride-forming element with mobile nitrogen not yet removed from the steel.

The method has been shown to be reliable for steels containing aluminium, silicon and titanium at 350—450°C [5—7] and vanadium at 350—440°C [8], and to be useful for steels containing niobium at 350°C [9]. Generally, the highest temperature within a recommended range is used to remove all the mobile nitrogen within the shortest time.

In the course of this work, it became clear that the extraction method with hydrogen might be extended to higher temperatures in order to determine the concentrations of the types of nitrogen left in a steel after removal of mobile nitrogen. Many carbon steels contain manganese and silicon along with a stronger deoxidizer such as aluminium or titanium. In such steels, combined nitrogen may exist as aluminium nitride or titantium nitride or carbonitride, and as manganese silicon nitride [7, 10]. The thermodynamic stability of these nitrides lies in the order TiN > AlN > $MnSiN_2$. Titanium nitride is stable at the temperature of molten iron [11]. Manganese silicon nitride is slightly dissociated at 600°C and the atomic nitrogen from it is completely removed from a steel as ammonia in a stream of hydrogen [7]. Therefore it should be possible to determine mobile nitrogen, manganese silicon nitride and titanium nitride in a steel containing only these types of nitrogen by collecting ammonia produced on the surface of millings of the steel in a stream of hydrogen first at 450°C and then at 600°C. The nitrogen left in the steel at 600°C should be in the form of titanium nitride or carbonitride and

is determined by difference when the total nitrogen content is known. Results will be presented to show that this is so.

It seemed possible that mobile nitrogen, manganese silicon nitride and aluminium nitride in a steel containing only these types of nitrogen could be determined in a similar way. However, aluminium nitride is less stable than titanium nitride and it was important to know that aluminium nitride is not dissociated in steels at 600°C if the method is to be reliable. Therefore an independent method for determining aluminium nitride in a series of steels containing aluminium and silicon was devised. Results will be presented to show that a hydrogen extraction method can be used to determine aluminium nitride by difference in such steels, when the total nitrogen content is known. The independent method for determining aluminium nitride was based on the relationship:

$$\text{Al as nitride} = \text{total Al} - \text{elemental Al} - \text{Al as oxide} \qquad (1)$$

The elemental aluminium was determined by dissolving the steel in a mixture of bromine and acetonitrile, filtering off undissolved precipitates, distilling off most of the bromine from the filtrate and determining the aluminium in the acetronitrile solution by atomic absorption spectrometry. This method was preferred to the Beeghly method for aluminium nitride, because of uncertainty about the complete solubility of manganese silicon nitride in bromine—methyl acetate mixtures [7].

A considerable amount of nitrogen was removed from some of the steels tested at 600°C in a stream of hydrogen, after prior removal of mobile nitrogen. In this study, it was not possible to identify the phase from which this nitrogen was dissociating at 600°C as manganese silicon nitride; therefore, this nitrogen will be referred to as nitrogen released at 600°C.

EXPERIMENTAL

Titanium steels

Preparation of the steels. The series of steels used was prepared in the Metallurgy Department from pure materials. The compositions of these steels are shown in Table 1; it can be seen that they fall into three groups. The final treatment of these steels involved hot rolling at 950°C and cooling in air.

Nitrogen determinations. Mobile nitrogen was determined by the extraction method with hydrogen at 440°C on fine millings [3]. The milling operations were undertaken very slowly to minimize any localized heating of the steel bars. When all the mobile nitrogen had been released and collected as ammonia after about 2 h, the temperature of the furnace was raised to 600°C and any further release of nitrogen as ammonia was recorded. Collection times of about 2 h were required. When the release of nitrogen at 600°C had ceased, the furnace temperature was further increased to 750°C to see if any more nitrogen would be released over a period of 2 h.

Microscopic examination of precipitates. In an attempt to identify the nitride phases present in the series of manganese—silicon—titanium steels,

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TABLE 1

Compositions of the manganese—silicon—titanium steels

Steel	C (%)	Mn (%)	Si (%)	Ti (%)	Total N (%)
1	0.041	3.64	0.42	—	0.010
2	0.028	3.42	0.38	0.019	0.011
3[a]	0.035	3.50	0.28	0.036	0.007
6	0.21	1.33	0.28	0.005	0.0034
7	0.21	1.35	0.30	0.015	0.0036
9	0.24	1.13	0.29	0.020	0.0045
12	0.20	1.58	0.29	0.016	0.010
11	0.21	1.74	0.33	0.027	0.010

[a] Also contained 0.12% chromium.

steels 1, 2 and 3 were examined, where appropriate, by optical microscopy in conjunction with electron microprobe analysis with lithium fluoride, pentaerythritol and stearate crystals, and by electron microscopy and electron diffraction. These latter techniques were applied to inclusions isolated from the steels after bromine—methyl acetate dissolution and examination of the particles on carbon films, and to carbon extraction replicas.

Aluminium steels

Preparation of the steels. The steels tested (Table 2) were specially prepared in a vacuum induction furnace from pure materials. The high-purity iron and graphite were melted and vacuum-degassed to remove carbon monoxide, before silicon, aluminium and manganese nitride were added. After preparation these steels were held at 1150°C for 1 h and cooled in the furnace.

Nitrogen determinations by extraction with hydrogen. Mobile nitrogen was determined at 450°C on fine millings [3]. Further release of nitrogen at 600°C and 750°C was examined as described for titanium steels.

TABLE 2

Compositions of the manganese—silicon—aluminium steels

Steel	C (%)	Si (%)	Mn (%)	Al (ppm)	O (ppm)	Total N (ppm)
A	0.13	0.32	0.93	<50	32	140
B	0.20	0.32	0.90	100	21	110
C	0.19	0.40	1.10	200	18	130
D	0.17	0.34	0.88	300	21	100
E	0.18	0.35	0.93	700	23	140
F	0.17	0.36	1.00	120	12	100
G	0.18	0.37	1.02	200	13	100
H	0.19	0.31	1.48	300	5	110

Determination of elemental aluminium. The steel sample (0.5 g) was dissolved in 15 ml of dry acetonitrile and 2 ml of dry bromine in a stoppered flask cooled in ice. Excess of bromine was removed by distillation, and the flask was cooled, stoppered and transferred to a dry glove-box. The solution was then filtered through Whatman GF/C glass fibre discs to remove any precipitate and made up to 50 ml in a graduated flask. It was necessary to work in the glove-box because aluminium bromide is readily hydrolysed by water vapour from the atmosphere.

The concentration of aluminium in the acetonitrile solution was determined with a Unicam SP90A atomic absorption spectrometer and nitrous oxide—acetylene flame at the aluminium 309.3-nm resonance line. The calibration graph was prepared from acetonitrile solutions that contained 1% (w/v) iron and aluminium in the range 2—10 μg ml^{-1}. These solutions were prepared by appropriate dilution of standard solutions of iron and aluminium in acetonitrile containing a stoichiometric excess of bromine.

RESULTS AND DISCUSSION

Titanium steels

For all 8 steels no further nitrogen was released at 750°C after collection of nitrogen as ammonia from steels heated first at 440°C and then at 600°C. The nitrogen remaining in the steels at 600°C and 750°C must therefore be in the form of the very stable titanium nitride or titanium carbonitride. The concentrations of the various types of nitrogen in these steels are shown in Table 3.

It should be noted that all of the nitrogen was removed from steel 1 by

TABLE 3

The concentrations of the various types of nitrogen in the manganese—silicon—titanium steels

Steel	Ti (ppm)	Total N (ppm) *A*	Mobile N released at 440°C (ppm) *B*[a]	Further N released at 600°C (ppm) *C*[a]	N as TiN or Ti (C, N) (ppm) $A-(B+C)$
1	—[b]	100	40	60	0
2	190	110	37	42	31
3	360	70	12	9	49
6	50	34	29	4	1
7	150	36	26	6	4
9	200	45	23	8	14
12	160	100	54	32	14
11	270	100	39	17	44

[a]Averages of two results agreeing within 5 ppm. [b]Not detected.

treatment with hydrogen at 440°C and 600°C; this steel contained no added titanium. Almost all the nitrogen was also released from steel 6, which contained a low concentration of titanium, after similar treatment. As expected, however, the concentration of titanium nitride or carbonitride in these steels increased as the concentration of titanium increased within any of the three groups.

When optical microscopy was used, titanium nitride particles were found in steels 2 and 3, occurring more frequently in steel 3 with the higher titanium concentration. The particles were very yellow in colour, indicating that they contained very little or no carbon [12]. Two such particles were shown by electron microprobe analysis to contain titanium and nitrogen, but no manganese or sulphur.

Inclusions isolated from steels 1, 2 and 3 after bromine—methyl acetate dissolution of the iron were examined by electron microscopy and diffraction but clear diffraction patterns were not found with steels 1 and 2. With steel 3 a good diffraction pattern was observed from one large particle; this pattern corresponded to a f.c.c. crystal with a unit cell length of 4.24 Å. The literature value for f.c.c. TiN is 4.235 Å [13], and undoubtedly the particle was a small secondary titanium nitride crystal.

Electron diffraction patterns could not be found from carbon replicas from steels 1, 2 and 3 that would correspond to a manganese silicon nitride phase. In the steels investigated, any precipitated phase containing silicon and nitrogen should be $MnSiN_2$ [10]. However, the heat treatment received by these samples was not such as to encourage the growth of even moderately sized crystals of this phase; the phase is probably present but only as submicroscopic particles. Certainly the release of nitrogen at 600°C from a steel, from which mobile nitrogen has already been removed, would be expected if the $MnSiN_2$ phase is present [7].

Aluminium steels

The concentrations of the various types of nitrogen in these steels obtained by the extraction method with hydrogen are shown in Table 4. The calculated standard deviation for all results in the last column was 7 ppm. The biggest contribution to the standard deviation of the results for nitrogen as aluminium nitride came from the results for total nitrogen, which were determined chemically by a Kjeldahl method.

It can be seen that as the Al:total N ratio increases, the mobile N:total N ratio decreases, as expected. The further nitrogen released at 600°C is probably produced by the breakdown of manganese silicon nitride as found by Kretschmer [7] for manganese—silicon—aluminium steels. Comparison of the results for further nitrogen released at 600°C for steels A, B and C shows that the concentration of this type of nitrogen increases as the concentration of aluminium nitride increases, provided that the atomic ratio of Al:total N<1. It appears that precipitation of aluminium nitride induces further precipitation of manganese silicon nitride, as noted by Okada et al. [14].

TABLE 4

The concentrations of the various types of nitrogen in the manganese—silicon—aluminium steels

Steel	Al (ppm)	Total N (ppm) K	Mobile N released at 450°C (ppm) L[a]	Further N released at 600°C (ppm) M[a]	Further N released at 750°C (ppm) N[a]	N as AlN (ppm) $K-(L+M)$
A	<50	140	105	23	<5	12
B	100	110	32	37	11	41
C	200	130	19	55	16	56
D	300	100	6	<5	<5	~94
E	700	140	<5	<5	<5	~140
F	120	100	29	44	16	27
G	200	100	13	41	11	46
H	300	110	3	4	3	103

[a] Averages of two results agreeing within 5 ppm.

Unlike the situation with the titanium steels, a little further nitrogen was released from the aluminium steels at 750°C. This nitrogen probably originated from slight breakdown of very fine particles of aluminium nitride [4]. Hence the nitrogen as aluminium nitride in these steels was calculated by using the equation: nitrogen as AlN = $K - (L + M)$. It seems most unlikely that any manganese silicon nitride remains undissociated after hydrogen is passed over steel millings for 2 h at 600°C because no nitrogen remained to be released at 750°C from the simple manganese—silicon steel 1 (see Table 3).

Verification of the above equation for nitrogen as AlN was obtained by determining the concentrations of aluminium nitride in these steels through an aluminium mass balance by making use of relation (1) and comparing these results with those in the last column of Table 4. These results are calculated and compared in Tables 5 and 6, respectively. The agreement between the results for nitrogen as aluminium nitride determined by these two independent methods is quite good, when the standard deviations are taken into consideration. This agreement verifies that the difference method after extraction with hydrogen is reliable for determining the concentration of nitrogen bound as aluminium nitride in carbon steels containing no other strong nitride-forming elements. It is much more convenient to use than the method based on an aluminium mass balance.

The Beeghly method for determining aluminium nitride as described by Swinburn [1] was applied to steels B and F with atomic ratios of total Al: total N << 1 to see if it would give a reliable result for aluminium nitride in the presence of manganese silicon nitride. However, the results were 53 ppm and 51 ppm of nitrogen as aluminium nitride in B and F, respectively, which are appreciably in excess of the results reported by the recommended methods in Tables 4 and 5. This indicates that manganese silicon nitride is not dissolved

TABLE 5

Determination of nitrogen as aluminium nitride in manganese—silicon—aluminium steels based on aluminium mass balance

Steel	O (ppm)	Total Al (ppm) X	Elemental Al (ppm) Y	Al bound as oxide (ppm) Z	Al for AlN (ppm) $X-(Y+Z)$	Nitrogen as AlN (ppm) $[X-(Y+Z)]\times\frac{14}{27}$
A	32	<50	<10	—	<50	<26
B	21	100	20	24	56	29 (12)[a]
C	18	200	70	20	110	57 (12)
D	21	300	105	24	171	89 (12)
E	23	700	335	26	339	176 (16)
F	12	120	40	14	66	34 (11)
G	13	200	80	15	105	54 (11)
H	5	300	140	6	154	80 (11)

[a]Calculated standard deviations in parenthesis. The biggest contribution to the standard deviation of the results for N as AlN comes from the results for total aluminium, which were determined by direct-reading arc—spark emission spectrometry.

TABLE 6

Comparison of the results for nitrogen as aluminium nitride determined by nitrogen mass balance and by aluminium mass balance

Steel		A	B	C	D	E	F	G	H
N as AlN (ppm)	N mass balance	12	41	56	≈94	≈140	27	46	103
	Al mass balance	<26	29	51	89	176	34	54	80

completely on treatment with bromine—methyl acetate solution and that undissolved manganese silicon nitride is broken down to produce ammonia in the Beeghly procedure. Similar results were reported by Kretschmer [7] and the Beeghly method should not be used for steels that may contain manganese silicon nitride.

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Studies on the Determination of Low Concentrations of Nitrogen in Gas Streams

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This work was undertaken with the aim of developing a method for the determination of mobile nitrogen in steel. Using mass spectrometry it has been shown qualitatively that when a steel sample is dissolved in a methyl acetate - bromine mixture as described by Beeghly,[1] the mobile nitrogen, consisting of atomic nitrogen present in the steel lattice and that released by the dissolution of iron and manganese nitrides, is evolved as nitrogen gas. Typically a steel will contain 1–50 $\mu g\ g^{-1}$ of mobile nitrogen. This means that at room temperature and atmospheric pressure the volume of nitrogen evolved from a 1-g sample is no more than 0.04 cm^3. The nitrogen has to be determined quantitatively after being swept out of the solution by a carrier gas. This has been attempted in three ways.

Titanium sponge heated to 950 °C will absorb nitrogen from an inert gas such as argon.[2] The amount of nitrogen absorbed can then be determined by a Kjeldahl method[3] with an indophenol blue colorimetric finish.[4] However, the amount of Specpure titanium required in order to achieve complete removal of nitrogen from argon was 10 g and the method was too expensive and time consuming for routine operation.

An iron catalyst will promote the reaction between nitrogen and hydrogen to give ammonia. This has been used by Tölg[5] for the microdetermination of nitrogen in organic compounds. In this study a commercial catalyst (BASF S6-10) based on iron oxide promoted with oxides of aluminium, calcium, magnesium and potassium was used. The ammonia produced was absorbed in a triethanolamine - hydrochloric acid buffer solution at pH 6.9 and determined potentiometrically using an ammonium ion-selective electrode by the method of Headridge and Long.[6]

Being exothermic, the reaction between nitrogen and hydrogen is favoured by low temperature. No catalyst that works efficiently at room temperature is known. The catalyst used in this instance has a working range of 400–550 °C. The reaction was carried out at atmospheric pressure. Fig. 1 shows a plot of percentage conversion of 50-μg nitrogen samples introduced into hydrogen streams against temperature for a 2-h collection period. The optimum temperature for the reaction is 450–460 °C, although even in this temperature range there is only 50–60% conversion. In order for this method to be applicable to the problem in hand the degree of conversion should preferably be not less than 95%.

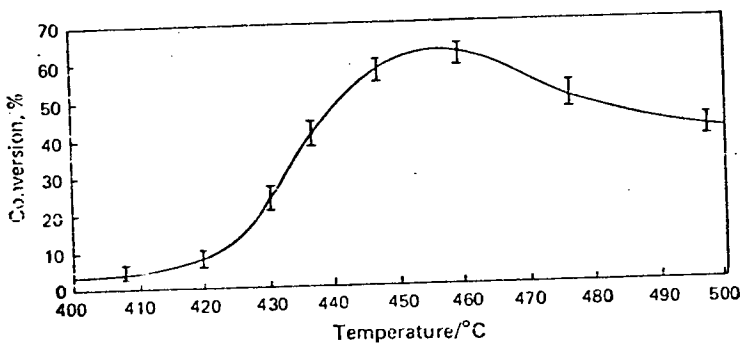

Fig. 1. Graph of percentage conversion of nitrogen to ammonia against temperature for a 2-h collection period.

Both of these methods involve the continuous removal from a carrier gas of nitrogen as it is produced by the dissolution of a steel sample. Hence they have to facilitate the complete removal of nitrogen from the carrier gas over a period of 20–30 min when the nitrogen has a continuously varying, though very small, concentration. The carrier gas itself must also be as free from nitrogen as possible because any nitrogen present will contribute to the blank. A method that involves the collection of the total amount of nitrogen evolved from the steel and its subsequent determination by a comparison technique is a possible alternative. Such a technique is gaseous refractometry.

When a coherent beam of light is split and then passed through two media with different refractive indices, an interference pattern results on recombination of the beams, because the speed of light is different in each medium. As the composition of one of the media is changed the pattern appears to move relative to a fixed position. The degree to which it moves is dependent on the change in composition of the medium. Fig. 2 illustrates a Rayleigh interferometer with which refractive indices can be measured after production of an interference pattern.

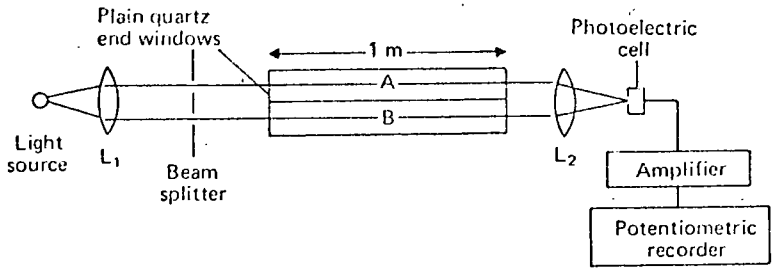

Fig. 2. Rayleigh interferometer. The light source is a 2-mW helium - neon laser, lens L_1 is the collimating lens and L_2 is the recombination lens. Cell A is the reference cell and cell B the sample cell. Each cell has a length of 1 m and a cross-sectional area of 1 cm^2.

Refractometers are commonly used as detectors in high-performance liquid chromatography as the range of refractive indices of liquids is very wide. However, the refractive indices of gases are all very similar and close to unity. For the application of this technique to the determination of mobile nitrogen in steel the carrier gas, in addition to being stable in the organic solvent - halogen mixture, should have a refractive index significantly different from that of nitrogen. For this reason, sulphur hexafluoride was chosen, with a refractive index of 1.000895 at S.T.P. for a wavelength of 589 nm, compared with 1.000296 for nitrogen and 1.000281 for argon.

For the determination the reference cell was continuously pumped to a vacuum while the sample cell was filled with different pressures of sulphur hexafluoride. This cell was then slowly evacuated and the number of fringes that moved over a fixed position was noted from the potentiometric recorder. The relationship between the number of fringes moved and the pressure of sulphur hexafluoride was found to be linear. Typically, a movement of one fringe corresponded to a pressure fall of 0.7 torr.

The sample cell was then filled with mixtures of sulphur hexafluoride and nitrogen of varying composition. The difference in number of fringes moved compared with the same pressure of pure sulphur hexafluoride was measured. Fig. 3 shows a graph of number of fringes moved against the molar fraction of nitrogen in the gas mixture. The limit of detection of the method, defined as twice the standard deviation of a series of determinations at or near the blank level, was 0.00015 molar fraction of nitrogen in sulphur hexafluoride. As 1.5 l of sulphur hexafluoride at about 600 torr are required to flush the nitrogen out of a solution of 1 g of steel in the organic solvent - halogen mixture, this corresponds to a detection limit of approximately 220 μg g^{-1} for mobile nitrogen in steel.

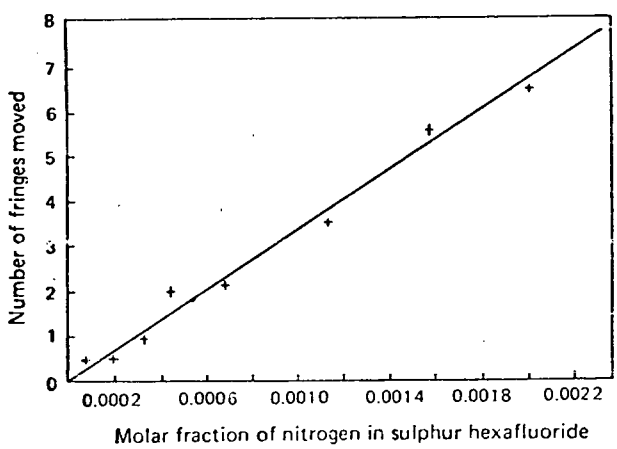

Fig. 3. Graph of number of fringes moved against molar fraction of nitrogen in sulphur hexafluoride.

The use of a 2-mW helium - neon laser as the light source in preference to a tungsten filament lamp and photoelectric detection in place of visual detection of fringe movement has improved the sensitivity of the method by approximately two orders of magnitude from that specified by the manufacturer. Further improvements would be expected if an electrical system of pressure measurement could be incorporated and the instrument could be isolated from extraneous vibrations, thus allowing easier and more accurate pressure measurements and enabling small fractions of fringes to be measured with confidence.

None of these three methods has yet proved good enough to be applicable to the determination of mobile nitrogen in steels. Currently, work is being done to improve the catalytic system, and the suggested improvements are being made to the refractometry apparatus. It is hoped that further work, based on the results of this initial investigation, will lead to the early solution of the problem of determining extremely small amounts of nitrogen released from steels by dissolution in organic solvent - halogen mixtures.

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Studies in Chemical Phase Analysis

Part I. Determination of the Solubilities of Elements in Certain Organic Solvent - Bromine Mixtures

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As part of a study on the quantitative separation of carbide, nitride, oxide and sulphide inclusions from metals, the solubilities of aluminium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, niobium, phosphorus, silicon, sulphur, tin, titanium, tungsten and vanadium have been determined at 25 °C in organic solvent - bromine mixtures (10 + 1 *V/V*) after refluxing. The solvents were methyl acetate, butyl acetate and acetonitrile. All of the above elements except lead, molybdenum, silicon and tungsten were appreciably or very soluble in these solvents. Molybdenum was sparingly soluble and the others almost insoluble.

Keywords: *Solubilities of elements*; *methyl acetate - bromine*; *butyl acetate - bromine*; *acetonitrile - bromine*

Metals often contain low concentrations of non-metals such as carbon, nitrogen, oxygen and sulphur, and the quantitative determination of these elements in metals is commonplace. However, the metallurgist is interested not only in the total concentration of a trace non-metal but also in the distribution of that element in the metal or alloy, including the concentrations of the various non-metallic phases containing that element. In order to obtain the latter information, these non-metallic phases usually have to be isolated from the metal matrix and a reagent may be used that will dissolve the metal and leave the non-metallic inclusions unattacked. The determination of the distribution of nitrogen in steel is of considerable importance.[1] In steels killed with aluminium, much of the nitrogen is present as aluminium nitride and Beeghly[2] pioneered the use of ester - bromine mixtures for the quantitative isolation of aluminium nitride from steels. Beeghly showed that aluminium nitride was insoluble in ester - bromine mixtures and indeed the use of methyl acetate - bromine has been widely adopted for the isolation of aluminium nitride from steels.[3] In a later article, Beeghly[4] states that the following metals are soluble in methyl acetate - bromine mixture: aluminium, beryllium, chromium, cobalt, iron, manganese, nickel, niobium, tin, titanium, uranium, vanadium, zinc and zirconium. If insoluble inclusions are to be cleanly separated from metals, it is necessary to know that the elements themselves have adequate solubilities in such solvents. If an element has a low solubility in an organic solvent - bromine mixture and is present in the metal in appreciable concentration, then it will accompany the insoluble inclusions in the residue and must be allowed for in a subsequent analytical scheme to determine the identities and amounts of every inclusion. Also, a knowledge of the solubilities of the elements (as bromides) enables one to calculate the minimum volume of solvent that is required to dissolve the bromides produced from a sample of metal and prevent unnecessary waste of solvent. Of course, enough bromine must be present in the volume of solvent selected to ensure that some will remain after all of the metals that react to produce soluble bromides have done so.

Therefore, it would be of considerable interest to know the actual solubilities of elements, carbides, nitrides, oxides and sulphides in anhydrous organic solvent - bromine mixtures to gauge the real potential of these solvents for chemical phase analysis and, in the first part of an extensive investigation, the solubilities of 17 elements have been determined in methyl acetate - bromine, butyl acetate - bromine and acetonitrile - bromine mixtures (all 10 + 1 *V/V*). Butyl acetate - bromine was included among these mixtures because it was felt that, at some time, it might be necessary to determine the concentration of certain trace elements in an ester by atomic-absorption spectrophotometry after dissolution of an alloy in ester - bromine and removal of excess of bromine by distillation. The boiling-points of bromine, methyl acetate and butyl acetate are 59, 57 and 126 °C, respectively. Acetonitrile - bromine

was investigated because acetonitrile is not readily attacked by oxidising agents and should be a better solvent than esters for the more ionic bromides, such as those of copper(II), manganese, cobalt and nickel.

Experimental

Reagents

Acetonitrile, methyl acetate and butyl acetate were Fisons laboratory-reagent grade materials. Bromine was Fisons analytical-reagent grade material.

Elements and alloys

Chromium, cobalt, iron, manganese, niobium and vanadium were Specpure metals supplied by Johnson Matthey Chemicals Ltd. Copper, lead, nickel, tin and titanium were of laboratory-reagent grade, supplied by Hopkin and Williams Ltd. Aluminium (AnalaR grade) and red phosphorus and sulphur (both laboratory-reagent grade) were obtained from BDH Chemicals Ltd.

Ferromolybdenum (48.6% molybdenum) and ferroniobium (62.7% niobium) were a gift from London and Scandinavian Metallurgical Co. Ltd. Ferrosilicon (75.0% silicon) and ferrotungsten (79.9% tungsten) were BCS 305/1 and BCS 242/2, respectively.

The physical forms of the elements were as follows: aluminium and nickel, wire; chromium, beads; tin, foil; lead, grains; copper, ferromolybdenum, ferrosilicon and red phosphorus, powder; cobalt, iron and nickel, sponge; ferroniobium and ferrotungsten, chips; and sulphur (flowers), crystals.

Purification and Drying of the Solvents

Acetonitrile. This was purified according to the method of Walter and Ramaley.[5]

Methyl acetate and butyl acetate. These were purified using standard procedures.[6]

Bromine. Shake equal volumes of bromine and concentrated sulphuric acid in a separating funnel. Separate the bromine and store in a stoppered bottle.

Determination of the Solubilities of Elements in the Organic Solvent - Bromine Mixtures

In all instances the proportions of organic solvent and bromine were 10 + 1 *V*/*V*. Solubilities are reported later as masses of elements in 100-ml volumes of solution. In effect, a solubility is the mass of element in 100 ml of solution saturated with its bromide, except where the bromide is so soluble that all of the bromine is reduced to bromide and the solution is not yet saturated, *e.g.*, iron in methyl acetate - bromine mixture.

General method

A 30-ml volume of an organic solvent - bromine mixture was placed in a 100-ml round-bottomed flask, to which was attached a reflux condenser and a calcium chloride drying tube. An amount of 300 mg of element or ferro-alloy was added to the flask. It was noted if there was any reaction in the cold, any vigorous reaction being controlled by immersing the flask in a cold bath of crushed ice and water. If there was not, the mixture was gently heated until a reaction was observed. In either instance, a reaction was allowed to go to completion. If no reaction was observed, the mixture was heated under reflux for 30 min, then allowed to cool. The solution was inspected to see if any solid remained undissolved.

Two situations could now exist: (*i*) some solid remained in the flask, indicating undissolved element or the formation of an insoluble bromide owing to saturation of the solvent mixture with the bromide, and (*ii*) all material was in solution. With case (*i*), 300 mg of element were added to the flask as a safeguard to ensure that solid would remain after a reflux of 30 min, which was then carried out. With case (*ii*), 300 mg of element were added to the flask and the solution was refluxed for 15 min unless the element dissolved at a lower temperature. If this sample dissolved, the same procedure was repeated as often as required until solid remained in the flask after reflux. This flask now corresponded to case (*i*) and the treatment outlined above was carried out.

The dissolution flask was removed and stoppered, then transferred into a water-bath at 25 °C and left for a minimum of 2 h. The solution was filtered off immediately after removing the flask from the water-bath using a Millipore filtration device containing a Whatman Glass Microfibre paper, type GF/F. Reduced pressure was produced in the collecting flask below the filter-paper to achieve rapid filtration. A volume of 10 or 20 ml of filtrate (20 ml for a less soluble element) was removed by pipette and placed in a 100-ml round-bottomed flask. With acetonitrile - bromine and methyl acetate - bromine mixtures the solvent was removed by evaporation on a steam-bath. With butyl acetate - bromine mixtures the solvent was removed at as low a temperature as possible by means of a heating mantle.

The residue was dissolved in dilute acid, often 0.1–0.2 M hydrochloric or nitric acid, the solution transferred into a calibrated flask and made up to the mark with water or dilute acid. With copper and molybdenum residues, the addition of acid and hydrogen peroxide (30% *m/V*) was necessary to effect solution. With the titanium residue, 8 M sulphuric acid was required and nitric acid - hydrofluoric acid solutions were needed to dissolve the niobium and tungsten residues. Because phosphorus tribromide and pentabromide and silicon and tin tetrabromides have low boiling-points (173, 106 with decomposition, 154 and 202 °C, respectively), 20 ml of filtrate (10 ml for tin and for butyl acetate only) were treated with 20 ml of water and left overnight to bring about hydrolysis before evaporation. The silicon residue was dissolved with a mixture of cold hydrofluoric and nitric acids, the tin residue with hydrochloric acid and the phosphorus residue with sulphuric acid, followed by treatment with chlorine and boiling. In some instances it was necessary to filter the solutions through Whatman No. 40 papers to separate them from small insoluble deposits of an organic nature.

The element content of each aqueous solution, except those from phosphorus and sulphur, was determined using a Unicam SP90 atomic-absorption spectrophotometer fitted with the appropriate hollow-cathode lamp and an air - acetylene or dinitrogen oxide - acetylene flame. Standard solutions for each calibration graph were prepared by dissolving the element or, with molybdenum, niobium, silicon and tungsten, the ferro-alloy in appropriate acids or acid mixtures and diluting each solution to a definite volume in a calibrated flask.

When determining the solubilities of molybdenum, niobium, silicon and tungsten in the organic solvent - bromine mixtures it was found that these elements were unreactive. Therefore, it was decided to dissolve ferro-alloys rather than the element, because iron is very soluble in these solvents and it was felt that the non-reactivity of the elements themselves could have resulted from a very stable but very thin coating of oxide. This was certainly so with niobium. Because ferro-alloys were used in the solubility studies of these four elements, it was necessary to arrange for iron also to be present in their standard solutions such that the concentration of iron in both the "unknown" and standard solutions would be identical for any particular element among these four.

The concentrations of phosphorus in the aqueous solutions prepared from the organic solvent - bromine mixture saturated with phosphorus tribromide and/or pentabromide were determined by molecular-absorption spectrophotometry using the molybdenum-blue method.[7] The approximate solubility of sulphur in the organic solvent - bromine mixtures was determined by adding 100-mg samples of sulphur to 30 ml of mixed solvents until it was observed that solid remained in the flasks after reflux.

Results

Reactivities of the Elements with Methyl Acetate - Bromine (10 + 1 *V/V*)

Iron and red phosphorus reacted violently in the cold. Cobalt, manganese, sulphur, tin and titanium also dissolved readily in the cold. Reaction with aluminium, chromium, copper, nickel and vanadium commenced after gentle heating. Lead was unreactive even on refluxing. Ferromolybdenum, ferroniobium, ferrosilicon and ferrotungsten reacted readily with the solvent mixture on warming but only niobium formed a fairly soluble bromide (see later).

Reactivities of the Elements with Butyl Acetate - Bromine (10 + 1 *V/V*)

Red phosphorus reacted violently in the cold. Iron, tin and titanium dissolved readily in the cold. Aluminium, chromium, cobalt, copper, manganese, nickel, sulphur and vanadium reacted after gentle heating. Lead and the ferro-alloys reacted in the same way as for methyl acetate - bromine.

Reactivities of the Elements with Acetonitrile - Bromine (10 + 1 *V/V*)

These were identical with the reactivities with methyl acetate - bromine except that nickel also dissolved readily in the cold.

Solubilities

The solubilities of the elements as anhydrous bromides are shown in Table I. These are expressed as solubilities of the elements at 25 °C after refluxing with the solvents as described under Experimental.

TABLE I

SOLUBILITY OF ELEMENTS IN ORGANIC SOLVENT - BROMINE MIXTURES (10 + 1 *V/V*) AT 25 °C AFTER REFLUXING WITH THE SOLVENT

Element	Solubility (g per 100 ml) in— Methyl acetate - bromine	Butyl acetate - bromine	Acetonitrile - bromine
Aluminium	3.1	2.8	3.4
Chromium	4.1	8.2	7.5
Cobalt	1.9	1.3	2.8
Copper	0.4	0.5	1.5
Iron	12.0	8.0	6.4
Lead	0.004	0.001	0.003
Manganese	2.8	0.7	3.4
Molybdenum*	0.10	0.12	0.12
Nickel	2.4	1.7	3.9
Niobium*	1.6	0.6	1.6
Phosphorus (red)	1.7	2.5	1.8
Silicon*	0.003	0.001	0.002
Sulphur	~1.5	~2.0	~1.5
Tin	4.5	2.8	3.7
Titanium	7.2	6.0	2.4
Tungsten*	<0.02	<0.01	<0.02
Vanadium	4.8	2.6	3.3

* Ferro-alloys were used.

Discussion

It can be seen from Table I that lead, silicon and tungsten have very low solubilities in all three solvent mixtures. Lead probably reacts with bromine to produce a surface coating of insoluble lead bromide. Lead bromide is sparingly soluble in water (0.84 g per 100 ml at 20 °C) Silicon tetrabromide would be expected to be soluble in these solvents but obviously it is not formed in these solvent mixtures. Molybdenum as ferromolybdenum dissolves in all of these solvent mixtures but its bromide is only sparingly soluble. The other elements have good or reasonably good solubilities in all of the solvent mixtures, although the methyl acetate - bromine and acetonitrile - bromine systems are overall slightly better solvents than butyl acetate - bromine mixture.

It will be noticed that cobalt, copper, manganese and nickel are indeed more soluble in acetonitrile - bromine than in the other two solvents. This is to be expected, as these are the elements that will form divalent bromides with more ionic bonding than trivalent and quadrivalent bromides such as those of aluminium and tin(IV). Acetonitrile, with a dielectric constant of 36.5 at 25 °C, is a much better co-ordinating solvent for ions than are methyl acetate and butyl acetate with dielectric constants of 6.7 (25 °C) and 5.0 (20 °C), respectively.

With methyl acetate - bromine, the very high solubility of iron can only be explained by iron dissolving as iron(II) bromide with no free bromine left in solution. Most, if not all, of the bromine has been used up by reaction with aluminium in the acetonitrile - bromine mixture. The high solubility of chromium in butyl acetate - bromine and acetonitrile - bromine mixtures indicates that the element has dissolved to produce a mixture of chromium(II) and chromium(III) bromides. Titanium, like iron, is very soluble in methyl acetate - bromine mixture and its high solubility must be explained by the titanium dissolving to produce titanium(II) and titanium(III) with no free bromine left in solution. In most other instances the saturated solution will contain unreacted bromine.

It would be of interest to know the actual formulae of the covalent bromides of molybdenum, niobium and vanadium isolated from saturated solutions of their bromides. In a related study, Cunion[8] has actually obtained $VBr_3.4CH_3CN$ from a saturated solution of vanadium bromide in acetonitrile prepared by dissolving vanadium metal in acetonitrile - bromine mixture.

The solubilities of the metal bromides (reported as dissolved metal) in the methyl acetate - bromine mixture may be slightly high owing to slight evaporation of the solvent mixture from the receiving flask below the filter, as the boiling-points of methyl acetate and bromine are 57 and 59 °C, respectively. This could lead to solutions that are slightly supersaturated with bromides.

This work has produced quantitative data that show that many elements are appreciably soluble in organic solvent - bromine mixtures. However, for useful phase analysis it is necessary to show that many of the compounds among the carbides, nitrides, oxides and sulphides found in metals are unattacked by organic solvent - bromine mixtures. The solubilities of such compounds in these mixtures will be reported in a later paper.

We thank the University of El-Fateh, Libya, for a studentship (for I.S.B.).

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Studies in Chemical Phase Analysis

Part II.* Determination of the Solubilities of Carbides, Nitrides, Oxides and Sulphides in Certain Organic Solvent - Bromine Mixtures

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As part of a study on the quantitative separation of carbide, nitride, oxide and sulphide inclusions from metals, the solubilities of five carbides, seven nitrides, sixteen oxides and eleven sulphides have been determined at 25 °C in methyl acetate - and acetonitrile - bromine mixtures (10 + 1 *V/V*) both after shaking at room temperature and after refluxing. Aluminium nitride and the carbides and nitrides of chromium, niobium, titanium and vanadium have low or very low solubilities, particularly in methyl acetate - bromine at room temperature, but iron carbide and iron and manganese nitrides are extensively decomposed, with the iron and manganese passing into solution. None of the oxides is more than sparingly soluble but most of the sulphides are appreciably soluble. Appropriate conditions are suggested for achieving a clean separation of oxides and stable carbides and nitrides from metals.

Keywords: *Solubilities of carbides, nitrides, oxides and sulphides; methyl acetate - bromine; acetonitrile - bromine*

For the isolation of non-metallic inclusions from metals the ideal solvent is one that will readily dissolve the metallic matrix and leave the inclusions unattacked. The use of ester - bromine mixtures for the quantitative isolation of aluminium nitride from steels was pioneered by Beeghly.[1] In steels that contained an excess of aluminium over nitrogen plus oxygen and that had been appropriately heat treated, he showed that virtually all of the nitrogen was recovered as insoluble aluminium nitride after dissolution of the steel in bromine - methyl acetate solvent. The nitrogen as aluminium nitride was determined as ammonia after a Kjeldahl distillation from alkaline solution. The method has since been widely used to determine aluminium nitride in steels.

The usefulness of bromine - methyl acetate mixtures to isolate aluminium nitride quantitatively from steels prompted investigations on the possibility of using such solvents to isolate other inclusions from steels. The results of these investigations are reported in several papers and reviews.[2–5] Of course, for success in these types of phase separations with steels, iron must be appreciably soluble in the solvent, and alloying metals at least moderately so. In Part I,[6] solubility studies were made using organic solvent - bromine mixtures (10 + 1 *V/V*) with refluxing. The organic solvents were methyl acetate, butyl acetate and acetonitrile and the solubilities of aluminium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, niobium, phosphorus, silicon, sulphur, tin, titanium, tungsten and vanadium were determined at 25 °C in the mixtures after refluxing. All of the elements except lead, molybdenum, silicon and tungsten were appreciably or very soluble in these solvent mixtures. Molybdenum was sparingly soluble and the others almost insoluble.

The inclusions of most interest are carbides, nitrides, oxides and sulphides. The general consensus is that most oxides are "insoluble" in ester - bromine mixtures, as are the more thermodynamically stable carbides and nitrides, but that sulphides are extensively decomposed by the solvents. With less stable nitrides and carbides such as Cr_2N[7,8] and Fe_3C[3,9] and with a few oxides such as FeO and MnO[5,10] there are conflicting reports as to whether these phases are soluble, partly soluble or insoluble. Therefore, it was felt that quantitative solubility data were needed for many of these compounds and this information is supplied in this paper.

The solubilities of certain carbides, nitrides, oxides and sulphides, which are known to occur as inclusions in metals, in organic solvent - bromine mixtures (10 + 1 *V/V*) are reported. Because methyl acetate - bromine and acetonitrile - bromine systems were over-all slightly better solvents for the elements than butyl acetate - bromine, it was decided to employ only

* For details of Part I of this series, see reference list, p. 226.

the former solvent mixtures in future work and to investigate the solubilities of the compounds at 25 °C both after refluxing and without refluxing. The potential of these solvent mixtures for the quantitative isolation of inclusions is also discussed.

Experimental

Reagents

Acetonitrile. Laboratory-reagent grade, Fisons.

Methyl acetate. Laboratory-reagent grade, Fisons.

Bromine. AnalaR grade, Fisons.

Metal compounds. The following were used: aluminium nitride, AlN, 99%, Koch-Light; aluminium oxide, Al_2O_3, AnalaR grade, BDH Chemicals; aluminium sulphide, Al_2S_3, technical grade, BDH Chemicals; chromium carbide, Cr_3C_2, Alpha Division; chromium nitride, Cr_2N, Metals Research; chromium(III) oxide, Cr_2O_3, laboratory-reagent grade, Fisons; chromium(III) sulphide, Cr_2S_3, 99%, Metals Research; cobalt(II) oxide, CoO, laboratory-reagent grade, Fisons; cobalt oxide, Co_3O_4, laboratory-reagent grade, BDH Chemicals; copper(I) oxide, Cu_2O, laboratory-reagent grade, BDH Chemicals; copper(II) oxide, CuO, AnalaR grade, BDH Chemicals; copper(II) sulphide, CuS, laboratory-reagent grade, Prestons; iron carbide, Fe_3C, 99%, Metals Research; iron nitride, $Fe_2N + Fe_4N$, Metals Research; iron(II) oxide, FeO, prepared by heating iron(II) oxalate in a stream of argon at 900 °C; iron(III) oxide, Fe_2O_3, laboratory-reagent grade, BDH Chemicals; iron(II) sulphide, FeS, technical grade, BDH Chemicals; manganese nitride, Metals Research (chemical analysis indicated that this was a mixture of Mn_2N and Mn_4N); manganese(II) oxide, MnO, Diamond Shamrock; manganese(IV) oxide, MnO_2, laboratory-reagent grade, Fisons; manganese sulphide, MnS, 99.9%, Metals Research; nickel(II) oxide, NiO; nickel sulphide, NiS, technical grade, BDH Chemicals; niobium carbide, NbC, high purity, Koch-Light; niobium nitride, NbN, 99.5%, Metals Research; niobium(V) oxide, Nb_2O_5, Specpure, Johnson Matthey; niobium sulphide, NbS, 99.8%, Metals Research; tin(II) oxide, SnO, laboratory-reagent grade, BDH Chemicals; tin(IV) oxide, SnO_2, laboratory-reagent grade, BDH Chemicals; tin(II) sulphide, SnS, laboratory-reagent grade, BDH Chemicals; tin(IV) sulphide, SnS_2, laboratory-reagent grade, BDH Chemicals; titanium carbide, TiC, 99.8%, Koch-Light; titanium nitride, TiN, 99%, Alpha Division; titanium(IV) oxide, TiO_2, laboratory-reagent grade, Fisons; titanium(IV) sulphide, TiS_2, 99.8%, Metals Research; vanadium carbide, VC, Alpha Products; vanadium nitride, VN, 99%, Metals Research; vanadium(III) sulphide, V_2S_3, 99.8%, Metals Research; vanadium(V) oxide, V_2O_5, laboratory-reagent grade, Fisons.

Any material not in the form of powder was crushed to powder before use. All oxides were heated in an oven at 105–120 °C for 1 h before use to ensure that they were dry.

Purification and Drying of the Solvents

Acetonitrile was purified according to the method of Walter and Ramaley[11] and methyl acetate by using a standard procedure.[12]

Bromine was purified by shaking equal volumes of bromine and concentrated sulphuric acid in a separating funnel, separating the bromine and storing it in a stoppered bottle.

Determination of the Solubilities of Compounds in Organic Solvent - Bromine Mixtures

In all instances the organic solvent - bromine ratio was 10 : 1 *V/V*. Solubilities are reported later as masses of metallic elements from the compounds in 100-ml volumes of solution. These masses were determined by atomic-absorption spectrophotometry.

Without refluxing

Place 30 ml of solvent mixture in a 100-ml round-bottomed flask, which with its stopper is fitted with glass hooks. Fit a reflux condenser and a calcium chloride drying tube to the flask to prevent the ingress of moist air. Add about 300 mg of compound to the flask and note any reaction. If a vigorous reaction is observed, control this reaction by immersing the flask in ice-cold water. When any reaction has subsided, add a further 300 mg of compound. If all of the material dissolves, continue to add 300-mg amounts of compound until all noticeable reaction ceases.

Remove the condenser and drying tube, stopper the flask, attach springs to the hooks and place the flasks in an electric shaker for 15 min, then place the flask in a thermostatically controlled water-bath at 25 °C overnight.

Quickly filter the solution through a disc of Whatman Glass Microfibre paper, type GF/F, in a dry Millipore filtration apparatus under reduced pressure. Pipette an appropriate volume of the filtrate in the range 10–20 ml into a beaker and evaporate the solvent by heating on a steam-bath. Dissolve the residue with a suitable acid and transfer the solution quantitatively into a calibrated flask for subsequent analysis by atomic-absorption spectrophotometry, after removing by filtration any small residue of insoluble organic material that may remain.

With refluxing

Employ the procedure that was used for determining the solubility of elements in the organic solvent - bromine mixtures as reported in Part I.[6]

Results

Reactivities of Compounds with Methyl Acetate - Bromine (10 + 1 V/V)

Manganese(II) sulphide reacted violently with the formation of a yellow solid. Iron carbide reacted vigorously and the sulphides of iron(II), tin(II), tin(IV), titanium(IV) and vanadium-(III) dissolved readily in the cold. Iron and manganese nitrides dissolved slowly in the cold. For the other compounds there was no noticeable reaction in the cold but some showed reaction on refluxing.

Reactivities of Compounds with Acetonitrile - Bromine (10 + 1 V/V)

Manganese(II) sulphide reacted violently with the formation of a yellow solid. Iron carbide reacted vigorously and manganese nitride and the sulphides of copper(II), iron(II), nickel, tin(II), tin(IV) and vanadium(III) reacted readily in the cold. Iron nitride and titanium(IV) sulphide dissolved slowly in the cold. Other compounds showed little reaction in the cold but some started to react when the mixture was heated under reflux.

Solubilities

The solubilities of the compounds are shown in Tables I–IV. These are expressed as solubilities of metallic elements from the compounds at 25 °C either after reaction at or near room temperature or after refluxing with the solvents. The metallic elements dissolve as anhydrous bromides when the compound is decomposed.

Discussion

It can be seen from Tables I and II that aluminium nitride and the carbides and nitrides of chromium, niobium, titanium and vanadium have very low solubilities in bromine - methyl acetate and can be described as "insoluble." Frequently they are slightly more soluble in bromine - acetonitrile and, as expected with both solvents, less compound dissolves at room temperature than after refluxing. On the other hand, iron carbide and nitride and manganese

TABLE I

SOLUBILITIES OF CARBIDES IN ORGANIC SOLVENT - BROMINE MIXTURES

	Solubility at 25 °C/g per 100 ml			
	Acetonitrile		Methyl acetate	
Compound	After refluxing	No refluxing	After refluxing	No refluxing
Chromium carbide, Cr_3C_2	0.007	0.002	0.005	0.001
Iron carbide, Fe_3C	5.5	4.7	2.5	1.9
Niobium carbide, NbC	0.03	<0.01	0.03	<0.01
Titanium carbide, TiC	0.016	0.008	0.016	0.008
Vanadium carbide, VC	0.24	0.04	0.05	0.02

TABLE II

SOLUBILITIES OF NITRIDES IN ORGANIC SOLVENT - BROMINE MIXTURES

Compound	Solubility at 25 °C/g per 100 ml			
	Acetonitrile		Methyl acetate	
	After refluxing	No refluxing	After refluxing	No refluxing
Aluminium nitride, AlN	0.009	0.007	0.008	0.003
Chromium nitride, Cr_2N	0.01	0.009	0.008	0.006
Iron nitride, Fe_2N + Fe_4N	3.2	1.8	1.3	1.1
Manganese nitride, Mn_2N + Mn_4N	2.3	1.6	2.1	1.1
Niobium nitride, NbN	0.03	<0.01	0.03	<0.01
Titanium nitride, TiN	0.010	0.008	0.010	0.008
Vanadium nitride, VN	0.04	0.03	0.03	0.02

nitride are decomposed in both solvents and the metallic moieties pass into solution as bromides. Presumably carbide is converted into carbon on decomposition and nitride into elemental nitrogen.

From Table III it can be seen that the solubilities of all oxides are low and none is more than sparingly soluble. Solubilities are often slightly greater in bromine - acetonitrile than in bromine - methyl acetate. This is probably because acetonitrile is a better co-ordinating solvent than methyl acetate. Again the solubilities are greater after refluxing. Obviously bromine - methyl acetate is a good solvent for isolating oxide inclusions from metals but slight solubility, particularly after refluxing, can be noticed with copper(I) and -(II) oxides, iron(II) oxide, manganese(IV) oxide and nickel(II) oxide.

As can be seen from Table IV, most sulphides have appreciable solubility in the solvent mixtures and those of copper(II), iron(II), manganese(II), nickel(II), tin(II) and tin(IV) are considerably more soluble in bromine - acetonitrile than in bromine - methyl acetate. Again this is because of the better co-ordinating ability of acetonitrile compared with methyl acetate. Only chromium(III) sulphide and niobium sulphide have low solubilities in these solvents. Metal sulphides dissolve to produce solutions of the metal and sulphur bromides. Clearly these organic solvent - bromine mixtures cannot be used to isolate most sulphide inclusions but they could be used to isolate oxides and many carbides and nitrides free from most sulphides. The solubility of manganese(II) sulphide appears to be low, particularly in bromine - methyl

TABLE III

SOLUBILITIES OF OXIDES IN ORGANIC SOLVENT - BROMINE MIXTURES

Compound	Solubility at 25 °C/g per 100 ml			
	Acetonitrile		Methyl acetate	
	After refluxing	No refluxing	After refluxing	No refluxing
Aluminium oxide	0.013	0.007	0.008	0.003
Chromium(III) oxide	0.003	0.002	0.004	0.003
Cobalt(II) oxide	0.03	0.02	0.09	0.04
Cobalt oxide, Co_3O_4	0.005	0.004	0.06	0.04
Copper(I) oxide	0.32	0.13	0.18	0.09
Copper(II) oxide	0.23	0.11	0.21	0.02
Iron(II) oxide	0.17	0.13	0.16	0.13
Iron(III) oxide	0.003	0.0006	0.002	0.0001
Manganese(II) oxide	0.09	—	0.06	—
Manganese(IV) oxide	0.30	0.09	0.18	0.08
Nickel(II) oxide	0.30	0.10	0.12	0.10
Niobium(V) oxide	0.03	<0.01	0.03	<0.01
Tin(II) oxide	0.04	0.02	0.01	0.008
Tin(V) oxide	0.016	0.013	0.008	0.005
Titanium(IV) oxide	0.006	0.004	0.006	0.004
Vanadium(V) oxide	0.06	0.02	0.07	0.02

TABLE IV

SOLUBILITIES OF SULPHIDES IN ORGANIC SOLVENT - BROMINE MIXTURES

	Solubility at 25 °C/g per 100 ml			
	Acetonitrile		Methyl acetate	
Compound	After refluxing	No refluxing	After refluxing	No refluxing
Aluminium sulphide	0.33	0.29	0.30	0.28
Chromium(III) sulphide	0.20	0.02	0.02	0.01
Copper(II) sulphide	1.4	1.0	0.23	0.10
Iron(II) sulphide	4.7	3.5	1.8	0.95
Manganese sulphide	2.0	1.2	0.22	0.02
Nickel sulphide	2.6	2.3	0.63	0.23
Niobium sulphide, NbS	0.06	0.03	0.04	0.03
Tin(II) sulphide	2.6	1.7	0.93	0.35
Tin(IV) sulphide	3.9	2.3	1.0	0.53
Titanium(IV) sulphide	0.72	0.40	1.5	0.68
Vanadium(III) sulphide	1.3	1.1	1.9	1.3

acetate without refluxing. However, as mentioned earlier, there is a violent reaction between manganese(II) sulphide and the solvent to produce a yellow solid of low solubility, which has not yet been characterised, and the solvent mixture cannot be used to isolate manganese(II) sulphide.

Considering all the solubilities in Tables I–IV, bromine - methyl acetate is preferred to bromine - acetonitrile for isolating inclusions. The total concentration of inclusions in a metal can be very low, sometimes not exceeding 0.01%. At first sight, the solubilities given in Tables I–III appear not to be low enough for achieving quantitative isolation of inclusions of oxides and the more stable carbides and nitrides. However, these solubilities were determined using conditions designed to encourage dissolution. Appreciable amounts of finely divided solids were shaken or refluxed with organic solvent - bromine mixtures (10 + 1 *V*/*V*). During the whole of the dissolution period the concentration of bromine remained high and the compounds and bromine were in contact for at least 3 h and often overnight.

In actual practice, the following conditions should apply.

(*i*) Calculate the amount of bromine required for the dissolution of the metallic phases in the mass of material taken and use an appropriate volume of methyl acetate plus bromine so that there is not more than a 10% excess of bromine but that enough methyl acetate is present to retain the soluble metal bromides in solution. Do not exceed a bromine to methyl acetate ratio of 1:10 *V*/*V*.

(*ii*) Carry out the dissolution at as low a temperature as possible in order to discourage dissolution of oxide and most carbide and nitride inclusions.

(*iii*) Filter the solution to collect the inclusions as soon as the metallic matrix has dissolved and wash the inclusions with pure solvent to remove trace amounts of bromine and bromides.

Under these conditions the solubilities of the "insoluble" oxides, carbides and nitrides should be sufficiently low to ensure their virtually quantitative isolation.

It is felt that the solubility data presented in this paper are a guide to which quantitative separations should be possible and which are unlikely to be successful in the field of chemical phase analysis. Until reliable methods for quantitative phase determinations have been devised using the solids themselves and microscopic techniques, chemical phase analysis following separation will continue to be necessary. However, it must be appreciated that the solubilities of carbides, nitrides and oxides, whether as inclusions or as powdered compounds, will be dependent on the size, surface area and density of the particles. No two materials are likely to be identical in all of these respects and a solubility determined for a particular sample of a compound is only a rough guide to the solubility for inclusions of the same compound in metals. Even so, the solubilities reported here should be helpful to those using methods of phase separation based on the dissolution of metals using organic solvent - bromine mixtures. With these data it should be possible to devise new separations and to confirm or view with caution some of the statements on solubilities that have appeared in the chemical literature.

It will be appreciated that only binary compounds as models for binary inclusions have been investigated in this study. Many binary inclusions exist in metals but many others contain more than two elements, for example, manganese silicon nitride, silicates, carbonitrides and carbosulphides. Because titanium carbide and nitride have been found to have very low solubilities in methyl acetate - bromine mixture, it can be assumed that titanium carbonitride will also have low solubility in this mixture. Similar predictions can be made with other carbonitrides. However, it is not possible to predict the solubilities of manganese silicon nitride or titanium carbosulphide from the data that have been presented. The solubilities of such compounds require further study.

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NOTE—Reference 6 is to Part I of this series.

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Section 5. Miscellaneous publications

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The Teaching of Microchemistry in British Universities

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Abstract

A review is given of the teaching to undergraduate students at British universities of analytical chemistry involving the use of samples of less than 5 mg. in weight and of solutions containing similar amounts of material. Other chemical operations involving samples of a similar size are discussed. Qualitative and quantitative analysis both by classical methods and by other methods, such as paper and gas chromatography, polarography, ion exchange, solvent extraction, and chemical microscopy, are considered. The teaching of methods for the elucidation of chemical structure involving microsamples, for example, x-ray powder diffraction, is also given attention.

In this paper, microchemistry is considered to be the chemistry of gaseous, liquid, or solid samples of up to 5 mg. in weight or of similar amounts of material in solution. For my purposes, the semimicroscale covers samples of 5–50 mg. in weight. Samples of greater than 50 mg. in weight are treated by macromethods. Most of the information in this paper has been obtained as a result of a questionnaire sent to chemistry departments in British Universities. Altogether 34 departments were covered and replies were received from 32 of these. The information applies to undergraduate teaching only. Organized courses of instruction are seldom given to postgraduate students in our universities.

Table I shows the categories into which microchemistry has been divided for the purpose of the survey. Each of these five categories will be considered in turn.

Table II contains information about the teaching of classical microanalysis.

Examples of exercises in quantitative inorganic microanalysis

TABLE I

Classical analysis	Inorganic quantitative Organic quantitative Inorganic qualitative Organic qualitative
Nonclassical methods	E.g., polarography
Microphysical methods	E.g., determination of molecular weights
Methods for the elucidation of structure	E.g., infrared spectrometry
Microsynthesis	

TABLE II

Item	No. of chemistry departments participating
Teaching of the use of the microbalance	7
Course in quantitative inorganic microanalysis by classical methods	5
Course in quantitative organic microanalysis	1

TABLE III

1. Nickel gravimetrically with dimethylglyoxime
2. Aluminum gravimetrically with 8-hydroxyquinoline
3. Copper gravimetrically by electrodeposition
4. Iron(II) volumetrically with dichromate using sodium diphenylamine sulfonate as indicator
5. Calcium volumetrically with EDTA using *o*-cresolphthalein complexone as indicator
6. Water by the Karl Fischer titration

taught in chemistry departments by classical methods are given in Table III.

Almost all university chemistry departments teach qualitative inorganic analysis on the semimicro scale. Qualitative organic analysis is generally taught on the macro scale, although a few departments analyze semimicro samples.

Table IV shows the nonclassical methods of analysis which are taught in our universities.

A few examples of the experiments carried out using certain of these techniques are given in Table V.

TABLE IV

Technique	No. of chemistry departments participating
Paper chromatography	27
Electrophoresis	4
Gas phase chromatography	14
Polarography	16
Flame photometry	9
Solvent extraction	10
Ion exchange	20
Chemical microscopy	4
Radiochemistry	14
Coulometric titration	7
Colorimetric determinations	15
Photometric titration	7
Potentiometric titration	2
Emission spectrography	2

TABLE V

Technique	Experiment
Paper chromatography	Separation and semiquantitative determination of lithium, sodium and potassium chlorides
Polarography	Determination of the half-wave potential for the reduction of lead(II) and the amperometric titration of lead with standard dichromate solution
Flame photometry	Determination of sodium and potassium in tap water
Chemical microscopy	Study of the system potassium chloride–magnesium chloride and the formation of carnallite
Coulometric titration	The titration of arsenite with electrically generated iodine
Colorimetric determination	Determination of traces of lead in water using dithizone

With regard to microphysical methods, most departments determine the melting point and boiling point of organic compounds on the micro scale. The determinations of other physical constants are usually taught with larger samples, although a few departments teach the determination of the molecular weights of micro samples by the Rast method.

Consideration in teaching is also given in most universities to the following methods for the elucidation of structure using micro samples, viz., infrared, raman, and ultraviolet spectroscopy; mass spectrometry; nuclear magnetic resonance and electron paramagnetic resonance spectroscopy; and x-ray powder photography. However, by no means all of our chemistry departments are able to offer undergraduate students practical instruction in these techniques. The estimated numbers of departments who offer practical instruction for certain of these techniques are given in Table VI.

TABLE VI

Technique	No. offering practical instruction
Infrared spectrometry	14
Mass spectrometry	3
X-ray powder photography	11

With regard to microsynthesis, the methods and techniques of microsynthesis are not taught to undergraduates, although some postgraduate research students gain experience in this type of work.

Finally, it must be stressed that the information given in this paper applies to the teaching of undergraduates. A postgraduate student working for an M.Sc. or Ph.D. degree may often employ microchemical techniques in his research, although the staff of the particular department in which he is working do not teach these techniques to their undergraduate students who are studying for the B.Sc. degree.

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THE SPECTROPHOTOMETRIC DETERMINATION OF PERRHENATE

A METHOD, which it is hoped will be described in a later paper, is being developed for the determination of rhenium in organic rhenium complexes containing nitrogen. The materials are completely oxidised by fusion with sodium peroxide in a micro Parr bomb, the melt is dissolved in water, and the solution is acidified and boiled to expel carbon dioxide, which gives a solution containing sodium, hydrogen, chloride, nitrate and perrhenate ions.

Perrhenate in solution can be determined gravimetrically as nitron or tetraphenylarsonium perrhenate,[1] but nitrate must be absent in the first of these determinations and interferes in the second unless present in extremely low concentrations.

A number of colorimetric methods for determining perrhenate are available. These include the formation of highly coloured rhenium complexes in reduced solutions with thiocyanate[2] and α-furildioxime,[3] the spectrophotometric determination of hexachlororhenate ion produced by reducing perrhenate in acid solution with hydrazine[4] or chromous chloride[5] and the colorimetric determination of perrhenate with 2:4-diphenylthiosemicarbazide.[6] Rhenium has also been determined spectrophotometrically as tetraphenylarsonium perrhenate in chloroform.[7] Nitrate ion is known to interfere in a number of these determinations.

Custers[8] has determined the absorption spectrum of potassium perrhenate and shown that the ion absorbs strongly in the ultra-violet region of the spectrum. The molar extinction coefficient was 3650 at a wavelength of 230 mμ, and it was indicated that Beer's law was obeyed over the range 221 to 313 mμ for concentrations between 0·02 and 0·0002 *M*.

The absorption of the perrhenate ion in the ultra-violet region does not appear to have been used in the determination of perrhenate, and investigations were therefore undertaken along these lines. The possible use of this method to determine perrhenate in the presence of nitrate was studied.

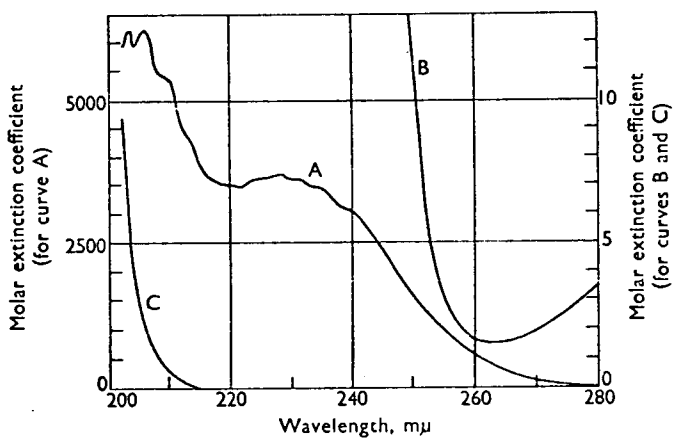

Fig. 1. Absorption spectra: curve A, potassium perrhenate; curve B, potassium nitrate; curve C, potassium chloride

The absorption spectra of the perrhenate, nitrate and chloride ions were determined in calibrated 1-cm quartz cells over the range 202 to 350 mμ, a Unicam SP500 spectrophotometer and solutions of Specpure potassium perrhenate, AnalaR potassium nitrate and AnalaR potassium chloride being used. These absorption spectra are shown in Fig. 1. The absorption spectrum of potassium perrhenate is in close agreement with the results of Custers and of Hindman and Wehner,[9] who used wavelengths longer than 215 mμ. The molar extinction coefficient is 3610 at 228 mμ and 6060 at 206 mμ. The chloride ion starts to absorb appreciably only at wavelengths shorter than 210 mμ, the molar extinction coefficient being 1·0 at 209 mμ. The nitrate ion has an absorption peak at 303 mμ ($\epsilon = 7{\cdot}2$) and a minimum at 264 mμ ($\epsilon = 1{\cdot}6$). There is a sharp rise in the value of the molar extinction coefficient for nitrate as the wavelength is further decreased.

The absorption peak at 228 mμ can be used in the determination of perrhenate in solutions containing no other ions that absorb appreciably at this wavelength. A straight line passing

through the origin is obtained when optical density is plotted against concentration over the range 0 to 50 p.p.m. of rhenium.

The optimum wavelength for the determination of perrhenate in the presence of both nitrate and chloride is 258 mμ. At this wavelength, the molar extinction coefficients for perrhenate and nitrate are 740 and 2·1. At 258 mμ, a straight line is obtained when optical density is plotted against concentration over the range 0 to 250 p.p.m. of rhenium in a 0·65 *M* solution of analytical-reagent grade sodium chloride. (The concentration of sodium chloride in the solutions from a sodium peroxide fusion is 0·65 *M*.) The line does not pass through the origin, but intercepts the optical-density axis at a value of 0·006, which corresponds to the very slight absorption of 0·65 *M* sodium chloride. When the absorption of the sodium chloride is taken into account, it is found that optical-density readings for perrhenate are depressed slightly (2 per cent.) in the presence of 0·65 *M* sodium chloride, but, when analysing solutions of unknown rhenium concentration, allowance for this effect can easily be made by constructing a standard graph, known amounts of rhenium in sodium chloride solution of that concentration being used.

The effect of potassium nitrate on the optical density of a solution containing 125 p.p.m. of rhenium in 0·65 *M* sodium chloride was studied, and the results were in agreement with those calculated from a knowledge of the molar extinction coefficients of nitrate and perrhenate at 258 mμ. In organic rhenium complexes, the ratio of nitrogen to rhenium will rarely exceed 8 to 1. Such a ratio will increase the optical-density reading for perrhenate by less than 2·5 per cent. If necessary, a correction can always be applied for the nitrate in the solution, as nitrogen in organic rhenium complexes can be readily determined by conventional methods of organic analysis. These results show that a method based on the absorption of the perrhenate ion will be satisfactory in the analysis of organic rhenium complexes.

In general, the proposed method, because of its ease of application, should be useful for the rapid determination of perrhenate in simple solutions.

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THE COMPLEXOMETRIC DETERMINATION OF MOLYBDENUM

LASSNER and Scharf[1] recently reported the determination of 5 to 30 mg of molybdenum^{VI} by a method involving reduction in sulphuric acid solution to molybdenum^{V} by hydrazine sulphate in presence of disodium ethylenediaminetetra-acetate (EDTA); the excess of EDTA was titrated against 0·05 *M* cupric sulphate at pH 4, with 1-(2-pyridylazo)-2-naphthol as indicator. This was the first mention of a satisfactory means of determining molybdenum directly by using EDTA, although indirect methods, based on the titration of calcium in calcium molybdate, had been described.[2,3]

Unaware that Lassner and Scharf were working on that problem, I have developed a similar method for determining molybdenum with EDTA by following up Pecsok and Sawyer's statement[4] that molybdenum^{V} and EDTA form in acid solutions a stable complex containing two atoms of molybdenum per molecule of EDTA. The method involves reduction of molybdate in hydrochloric acid solution by hydrazine sulphate[5] to molybdenum^{V}. The molybdenum^{V} - EDTA complex is formed, and the excess of EDTA is titrated against zinc chloride solution at pH approximately 4·2, alizarin complexone[6] being used as indicator. When photometric titration and 0·01 *M* solutions of EDTA and zinc chloride were used, from 1 to 11 mg of molybdenum were satisfactorily determined with a maximum error of $\pm$0·05 mg.

EXPERIMENTAL

An attempt was made to titrate the excess of EDTA over the amount required to react with the molybdenum^{V} formed on reduction by hydrazine sulphate against zinc chloride solution. The titration was carried out at pH 5·3, and xylenol orange was used as indicator, since its colour change is superior to those of most other indicators.[7] However, results were low when amounts between 1 and 10 mg of molybdenum were determined with 0·01 *M* zinc chloride as titrant (about

97 per cent. of the molybdenum present was found). The low results were caused by oxidation of about 3 per cent. of the molybdenum^{V} - EDTA complex at pH 5·3 before the excess of EDTA could be titrated. This oxidation was not brought about by atmospheric oxygen, since identical results were obtained when a solution containing 9·60 mg of molybdenum^{V} prepared by passing a solution of sodium molybdate through a silver reductor[8] was analysed by the above-mentioned complexometric method and by a method involving oxidation to molybdenum^{VI} by ceric sulphate solution.[8] Pecsok and Sawyer have also reported that the molybdenum^{V} - EDTA complex is stable to aerial oxidation below pH 7.

The low results at pH 5·3 seem to be associated with the hydrazine sulphate. When the concentration of this substance in the solution is increased ten-fold, the negative error is also increased (about 95 per cent. of the molybdenum present was found). Hydrazine is known to react with dissolved oxygen in weakly alkaline solutions[9] to produce hydrogen peroxide, and it may be that traces of hydrogen peroxide are formed even at pH 5·3. The hydrogen peroxide would then oxidise the molybdenum^{V} - EDTA complex and so give rise to low results. For this reason it was necessary to carry out the titration with zinc chloride solution at a lower pH. However, it was found that xylenol orange would not give a satisfactory end-point below pH 5·0, and therefore alizarin complexone[6] was used. A titration in a solution buffered at pH 5·3 would probably be satisfactory with xylenol orange as indicator if a reducing agent other than hydrazine sulphate could be found. Sulphur dioxide, hydroxylamine hydrochloride and ascorbic acid were tried as reducing agents, but none gave quantitative reduction of molybdenum^{VI} to molybdenum^{V}.

Method

Apparatus—

An E.E.L. titrator (Evans Electroselenium Ltd.) was used, although most filter photometers and spectrophotometers could be adapted for the photometric titrations.

The calibrated flasks used in preparing the standard solutions and the 10-ml microburette used for the titrations were of NPL grade A; other graduated glassware was of grade B.

Reagents—

All materials should be of analytical-reagent grade. The standard and EDTA solutions should be stored in polythene bottles.

Standard sodium molybdate solution—Prepare a solution containing about 0·25 g (accurately weighed) of sodium molybdate dihydrate per 100 ml; this solution is approximately 0·01 *M*. The solute used had a purity of 100·0 per cent., and its molybdenum content was determined by precipitation as lead molybdate.[10]

Standard zinc chloride solution—Dissolve about 0·65 g (accurately weighed) of zinc shot by heating with dilute hydrochloric acid. Evaporate the solution to the first appearance of solid, dissolve the residue in distilled water, and dilute to exactly 100 ml. Dilute 10 ml of this solution to 100 ml.

EDTA solution—Prepare a solution containing about 0·93 g of disodium ethylenediaminetetra-acetate dihydrate per 250 ml.

Buffer solution—Prepare a solution containing 45·9 g of sodium acetate trihydrate per 100 ml.

Hydrazine sulphate solution, saturated, aqueous.

Indicator solution, 0·5 per cent.—Treat 100 mg of alizarin complexone (obtainable from Hopkin and Williams Ltd.) with 2 drops of concentrated ammonia solution and then 7 to 8 drops of 20 per cent. w/v ammonium acetate solution, and dilute to 20 ml.

Procedure—

Place the molybdate solution (approximately neutral) containing 1 to 11 mg of molybdenum in a 50-ml beaker, and adjust its volume to about 10 ml. By pipette, add 1 ml each of concentrated hydrochloric acid and hydrazine sulphate solution. Heat to 95° C, and maintain at this temperature for 5 minutes. Cool, add 10 ml of EDTA solution, by pipette, and transfer to a 50-ml sample holder for the E.E.L. titrator. Insert the stirring rod, and set the stirrer in motion. By pipette, place 5 ml of buffer solution in the sample holder, and add 5 drops of indicator solution.

With use of an Ilford No. 604 filter, set the galvanometer reading (relative optical density scale) to about 8, and titrate the solution with standard zinc chloride solution added from a 10-ml microburette. When the galvanometer readings cease to decrease (dilution effect), take readings at 0·2-ml intervals until the reading begins to increase. Continue to record readings at more

frequent intervals until a further 2 ml of titrant have been added. Plot a graph of galvanometer readings against volume of titrant added. Extend forward the horizontal base line passing through the lowest galvanometer reading, and extend downwards the line of the steepest part of the curve until it intersects the horizontal base line; the intersection marks the end-point. Typical curves are shown in Fig. 1.

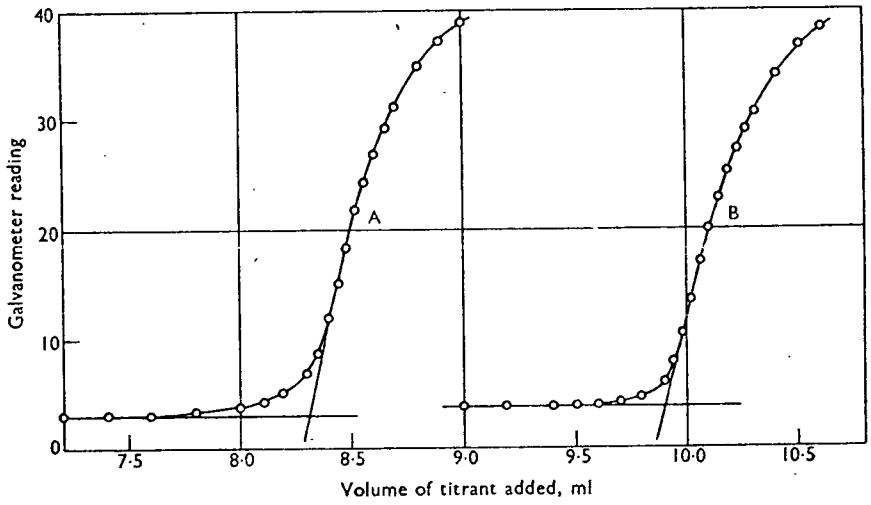

Fig. 1. Titration curves: curve A, 3·21 mg of molybdenum^{VI} *plus* 10 ml of EDTA solution (sample) against 0·01050 *M* zinc chloride; curve B, 10 ml of EDTA solution (blank) against 0·01050 *M* zinc chloride

Carry out the same procedure with a blank solution containing no molybdate. (This solution need not be heated to 95° C after the hydrazine sulphate solution has been added.) Subtract the titre for the sample solution from that for the blank solution to obtain the volume of standard zinc chloride solution equivalent to the molybdenum taken.

0·5 ml of 0·01 *M* zinc chloride ≡ 0·9595 mg of molybdenum.

Discussion of the Method

Typical results by the proposed method were—

Molybdenum present, mg	..	1·06	3·21	5·51	7·29	10·65
Molybdenum found, mg	..	1·09	3·20	5·56	7·26	10·61
Error, mg		+0·03	−0·01	+0·05	−0·03	−0·04

The procedure described above can, of course, be used only for pure molybdate solutions or solutions containing only alkali or alkaline-earth metals in addition to molybdate. It will require modification if it is to be used for determining molybdenum in presence of metals other than those just mentioned.

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LABORATORY METHODS
MECHANICAL : CHEMICAL : PHYSICAL : METALLOGRAPHIC
INSTRUMENTS AND MATERIALS

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The Determination of Low Concentrations of Oxygen in Steels and Nickel-Base Alloys using Vacuum Fusion followed by Mass Spectrometry

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A mass spectrometric method following vacuum fusion has been employed for the determination of 4 to 50 p.p.m. of oxygen in steels and nickel-base alloys. The limit of detection for oxygen was 0·15 μg. but the full sensitivity of the technique was not exploited because no alloys of oxygen content lower than 4 p.p.m. were available. Data on the precision of the mass spectrometric determinations are reported and discussed. Generally there is good agreement between results obtained by the mass spectrometric finish and conventional vacuum fusion followed by gas pressure measurement, but the mass spectrometric method is less involved and much more sensitive.

FOR vacuum melted steels and nickel-base alloys the oxygen contents are frequently below 20 p.p.m. and sometimes below 5 p.p.m. With conventional vacuum fusion equipment for oxygen determination, the weights of evolved gases are determined using a variety of methods, e.g. transducer pressure measurement, infrared absorption or thermal conductivity. However with such equipment the limit of detection for oxygen is usually > 1 p.p.m. Therefore it was considered that an appreciably more sensitive method would be desirable for the determination of such low levels of oxygen. Aspinal[1] has described equipment for vacuum fusion analysis with a mass spectrometer and has determined the oxygen contents of standard irons and stainless steels within the concentration ranges of 50–120 p.p.m. and 35–60 p.p.m., respectively, with a relative standard deviation of about 5%. However, the limit of detection for oxygen with his equipment is reported as 0·1 μg. of oxygen, which for a 1 g. sample is 0·1 p.p.m. Therefore it was decided to investigate the application of equipment similar to Aspinal's to oxygen determinations at concentrations as low as 4 p.p.m. Results for some 640 oxygen determinations in ferrous materials and nickel-base alloys are reported in this paper.

Mass Spectrometric Apparatus

The apparatus can be conveniently described in three parts, namely the furnace section, the gas handling section and the mass spectrometer section, and each of these are dealt with in turn. A block diagram of the complete vacuum fusion—mass spectrometric apparatus is shown in Fig. 1.

Furnace Section

A diagram of the crucible arrangement in the furnace is shown in Fig. 2. A commercial vacuum fusion furnace was used (Wild Barfield, Ltd.). Fine graphite powder was lightly packed in the silica crucible (6½ in. × 1½ in.) to a depth of about two inches. The graphite funnel was slid into the neck of the graphite crucible (4 in. × 1 in.; Cromil, Piercy, Ltd.), which was then placed in the silica crucible, such that the top edge of the funnel stood proud by about ¼ in. The gap between the two crucibles was then loosely packed with fine graphite powder. A graphite splash guard, 1½ in. deep, was placed on top of the funnel. The outer silica crucible contained a small hole on either side, near its top edge, so that it could be suspended by means of platinum wire clips from glass lugs in the upper part of the furnace tube.

After the crucible assembly had been placed in position, a ground glass plug was fitted into the bottom of the furnace tube, the seal being made with hard grade vacuum grease (Edwards High Vacuum, Ltd.). The top section of the furnace tube contained three side arms (only one is shown in Fig. 2), providing storage space for samples during the evacuation and subsequent outgassing of the furnace. One of these arms contained a sample lock, through which samples could be introduced into the apparatus during the course of a run of sample analyses. Samples were fed into the furnace one at a time with the aid of a magnet, a short bar of magnetic material being used as a pusher for the introduction of non-magnetic samples. The top of the furnace tube was closed with a ground glass joint having a reflecting prism cemented across its upper edge, hard grade vacuum

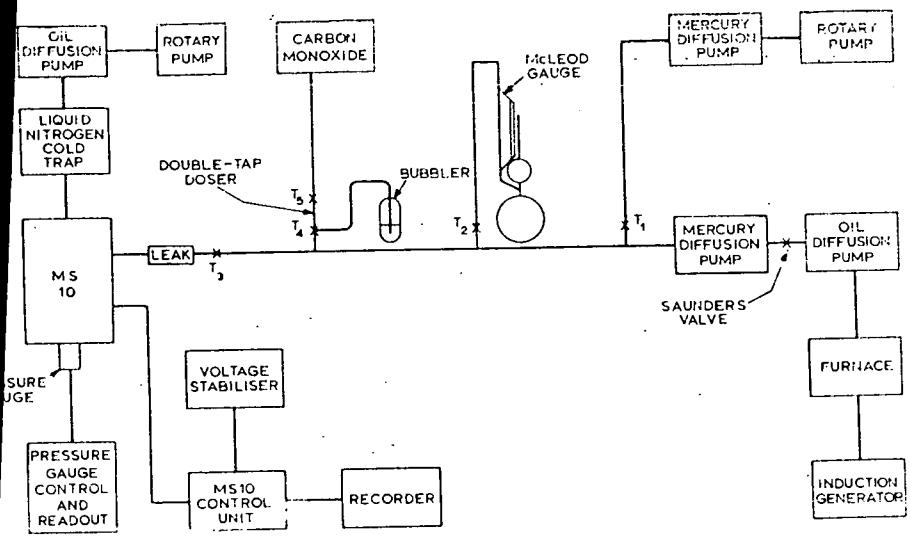

Fig. 1.—Block diagram of mass spectrometric vacuum fusion apparatus.

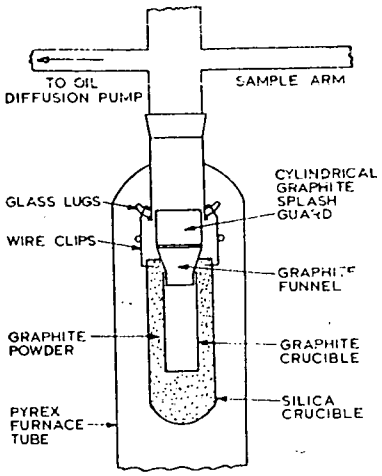

Fig. 2.—Crucible arrangement in the furnace.

grease being used to obtain a good seal from the ground glass joint. All other joints in the furnace were sealed with Apiezon W vacuum wax. The reflecting prism enabled the crucible to be viewed with a disappearing filament optical pyrometer (Leeds & Northrup, Ltd.) for temperature measurement.

The furnace tube was mounted concentrically within a water cooled induction coil of a 12 kW. induction generator (Radyne, Ltd.). The gases evolved from the furnace were transferred through the Pyrex side arm to the gas handling section by means of an A.E.I. O33C oil diffusion pump containing silicone 704 oil (Edwards).

Gas Handling Section

This consisted essentially of a long glass analyser tube, from which various facilities branched. The gases evolved from the furnace entered this section through a Saunders valve, which was attached to the backing side of the O33C oil diffusion pump in the furnace section. This Saunders valve was connected, by means of a bent Quickfit adaptor to a Q 20 mercury diffusion pump (Leybold, Heraus, Ltd.), which pumped the gases into the main analyser tube. The end of this tube was joined, via a glass-to-metal seal, to a standard porous plug leak (MS 10 Accessory X23), which diffused a minute proportion of the gas into the ionisation chamber of an A.E.I. MS 10 mass spectrometer. In early runs the Q 20 mercury diffusion pump was not used between the furnace section and the analyser tube, the oil diffusion pump alone being employed. However, when examining samples which contained appreciable amounts of gases, the critical backing pressure of the oil diffusion pump was such that quantitative extraction could not be achieved and, therefore, it was decided to augment the oil diffusion pump with a Q 20 mercury diffusion pump.

The gas handling section included a McLeod gauge, which could be excluded by means of a glass tap. The use of this tap provided two volumes in which the evolved gases could be contained. These were 204 ml. without the McLeod gauge and 426 ml. with the McLeod gauge. The McLeod gauge was used during the calibrating procedures to measure the pressure of the calibrating gas, which was introduced into the analyser tube via a double-tap doser. This was a calibrated volume of 55 μl. between two glass taps T_4 and T_5. All glass taps except T_1 were lubricated with Apiezon L grease. Edwards hard grade vacuum grease was used with T_1.

The gas handling section was pumped out by a 2M4 mercury diffusion pump (Edwards), backed by an Edwards 1SC 50 rotary pump.

Mass Spectrometer Section

The instrument used was the A.E.I. MS 10 mass spectrometer, a 5 cm. radius, 180° deflection instrument, which consisted essentially of an ionisation chamber surrounded by a magnet and containing an ion collector, and an electronic control unit with amplifier. The mains supply to the control unit was smoothed by an "Advance Volstat" voltage stabiliser (Advance Electronics, Ltd.).

The ionisation chamber was pumped out by a cold-trapped A.E.I. O33C oil diffusion pump containing Apiezon BW oil, backed by an Edwards 1SC 50 rotary pump. The output from the detector of the ionisation chamber (the ion current) was fed to the control unit, where it was amplified and displayed on both a meter and chart recorder. The pressure inside the ionisation chamber was measured with an N.G.N. Thermion ionisation gauge.

The amplifier had seven sensitivity settings covering ion currents between 10^{-10} and 10^{-13} A. for full scale deflection. These sensitivities were in the ratios 1,000: 250 : 100 : 25 : 10 : 2·5 : 1. Sensitivity 1,000 gave full scale deflection for an ion current of 10^{-10} A., whilst full scale deflection was achieved on sensitivity 1 with an ion current of 10^{-13} A.

Before operating the mass spectrometer, baking of the ionisation chamber was undertaken with the rotary pump in operation to remove adsorbed gases from the inner surfaces of the metal chamber. This was done by removing the magnet and the electrical connections to the unit, and fitting three 110 V. electrical band heaters around the flanges of the chamber. By this means, the unit was heated to a temperature of approximately 200° C. After baking for a minimum of twelve hours, the cold trap was filled with liquid nitrogen and the band-heaters switched off. When the chamber had cooled, the heaters were removed, the magnet and electrical connections replaced, and the oil diffusion pump

ched on. The liquid nitrogen cold trap was main-ed at all times, except during bake-out, the ionisation nber being left on bake-out when it was left ttended at the weekends.

he mass spectrometer was always operated with a current of 50 μA.

or oxygen determination in alloys, a mass to charge o of 12 was selected on the mass spectrometer for the owing reason. In vacuum fusion equipment the gen, nitrogen and hydrogen in alloys are released as on monoxide, nitrogen and hydrogen. Because the lecular weights of carbon monoxide and nitrogen are h 28, the amount of carbon monoxide released, which quivalent to the oxygen content of an alloy, cannot determined in the mass spectrometer at a mass to rge ratio of 28 but is determined at a ratio of 12 responding to the ion C^+ (mass 12) which, compared CO^+ (mass 28), is produced to the extent of about in the mass spectrometer.[1]

Preparation of Calibration Graphs for Oxygen

These were prepared as follows. After baking out the isation chamber with tap T_3 closed, switch on the ss spectrometer oil diffusion pump as described in the evious section and pump down to constant operating sidual pressure (preferably $<10^{-5}$ torr). Close tap T_4 d the Saunders valve, open taps T_1 and T_2, and pump t the gas handling section. Close tap T_1 and fill the uble-tap doser with spectrally pure carbon monoxide ritish Oxygen Co., Ltd.) at atmospheric pressure by ssing the gas through tap T_4 to the atmosphere rough a bubbler with appropriate control of flow rate. ose tap T_5 and reposition tap T_1 so that the carbon onoxide is introduced into the gas handling section. By ppropriate use of the taps T_4 and T_5 introduce a second μl. volume of carbon monoxide into the gas handling ction and close tap T_4. Switch to a sensitivity setting 1 on the mass spectrometer, switch on the recorder nd peak up on mass number 12. Open tap T_3. The pen hould go just off the recorder scale. Carefully open tap $_1$ very slightly until the pen comes back on to the scale nd almost a full scale deflection is obtained. Close tap $_1$, measure this deflection and the gas pressure on the McLeod gauge. The deflection corrected for background s proportional to the pressure of carbon monoxide in he gas handling section. By very careful control of tap $_1$ pump out progressively, eight or nine times, small mounts of carbon monoxide from the gas handling ection and measure the gas pressure and recorder eading between each pumping. Knowing the volume of he gas handling section, convert the gas pressures to weights of oxygen and draw a calibration graph of ecorder reading corrected for background versus weight f oxygen. This will be a straight line passing through he origin.

In a similar way prepare calibration graphs for the sensitivity settings of 2·5 and 10.

Analysis of Metal Samples

Cut the samples to size (usually 0·8 to 1·2 g.) on a grinding wheel and file them thoroughly to remove surface oxidation caused by the cutting. Then degrease the samples in acetone followed by ether and weigh them. With the graphite crucible, funnel and splash guard, and the side arms in position introduce the samples into the side arms manipulating them with a magnet. Close taps T_3 and T_4, open the Saunders valve, and switch on the rotary pump in the gas handling section. Slightly open tap T_1 and evacuate the apparatus slowly over a period of at least 20 minutes to avoid the possibility of graphite powder being sucked out of the silica crucible. When the McLeod gauge indicates that the pressure is less than 0·1 torr, switch on the 2M4 mercury diffusion pump. The pressure quickly falls to <0·001 torr. If the system is free from leaks, switch on the Q 20 mercury diffusion pump and the O33C oil diffusion pump. Commence the crucible outgassing procedure.

Switch on the induction heater and apply a very low rate of heating for 20 min. Increase the rate of heating in small steps over a further period of 20 min. When the graphite crucible achieves a dull red colour, increase the rate of heating substantially until a crucible temperature of 1950° C. is attained. Outgas at this temperature for 2 hours. Reduce the temperature of the crucible to 1700° C. Close taps T_1 and T_2, open tap T_3 and set the mass spectrometer controls for the determination of the blank rate using the same conditions as employed for the calibration graph with sensitivity setting 1. The recorder reading increases slowly due to minute traces of carbon monoxide still being pumped from the furnace section.

Introduce a sample of iron-base metal into the crucible by means of a magnet and collect the evolved gases for a period of 4 minutes whilst the rate of gas evolution is followed on the chart recorder. If necessary use a sensitivity setting of 2·5 or 10 to keep the pen on the recorder chart or open tap T_2 to increase the volume in the gas handling section. The rate of evolution of carbon monoxide returns to the blank rate in 3 minutes.

Measure the height of the step and read-off from the appropriate calibration graph the weight of oxygen producing this step. If necessary correct the chart reading if the larger volume was used. Open tap T_1 and pump out all of the collected gas from the gas handling section. In a similar way introduce the other samples in turn to the graphite crucible.

If samples of nickel-base alloys are to be analysed, it is essential to ensure that the ratio of iron to nickel in the crucible is in excess of 3 to 1.

Transducer Pressure Measurement Equipment

The equipment used for comparative purposes was a conventional vacuum fusion apparatus in which a transducer was used for pressure measurements. It was based on an apparatus in use at the Research and Development Department, Swinden House Laboratories, British Steel Corporation.[2] The evolved gases were passed over heated cupric oxide to convert carbon monoxide and hydrogen to carbon dioxide and water vapour respectively. The water vapour was absorbed in a phosphorus pentoxide tube, the pressure of the other gases determined and the carbon dioxide frozen out in a liquid nitrogen trap. The pressure of residual gas (mainly nitrogen) was again determined. The difference in pressures is proportional to the weight of oxygen in the sample.

Results

The calibration graphs for oxygen were straight lines through the origin. On the most sensitive setting of 1, 10 μg. of oxygen corresponded to 60 chart divisions. The slopes of the calibration graphs did not change by more than 2% during the time of this study.

TABLE I.—THE COMPOSITION OF ANALYSED SAMPLES

Sample	Specification Code	Composition (%)
106	EN31	1 C, 1·5 Cr
31, B2 and B3	Plain C Steel	1·5 C
34	EN 31	1 C, 1 Cr
Z 28 and Z 29	648	17 Ni, 8 Co, 5 Mo, 0·5 Ti
Z 39	448	10 Cr, 0·75 Ni, 0·5 Mo, 0·5 Nb
Z 50	G 85	19 Cr, 13·5 Co, 4 Mo, 3 Ti, 1·5 Al
VA 6976 and VA 6977	18/4/1	18 W, 4 Cr, 1 V
VA 7866	S 82	4 Ni, 1 Cr, 0·2 C
BES and TES	HCM 3	3 Cr, 1 Mo, 0·2 V
ZR 8/C	—	Zone refined pure iron
Z 31	688	45 Ni, 12 Cr, 5 Mo, 3 Ti, 0·5 Al
Z 47 and 48	Nim 90	Ni base, 20 Cr, 17 Co, 3 Ti, 1·5 Al
H 2589	G 79	Ni base, 13·5 Cr, 4·5 Mo, 2 Nb, 6 Al, 1 Ti

Results for the mass spectrometric determination of oxygen in iron-base materials (mainly steels) and in nickel-base alloys, whose compositions are shown in Table I, are given in Tables II and III. Where possible they are compared with the results obtained by transducer pressure measurement.

The mass spectrometric apparatus had a higher sensitivity than the transducer equipment, the limits of detection for the two techniques being in the order of 0·15 μg. and 1·5 μg. of oxygen, respectively. The furnace blank at 1700° C. ranged from 0·5 to 2·0 μg. of oxygen and was generally in the region of 1·0–1·3 μg. of oxygen for a 4 minute collection period.

Samples analysed with the mass spectrometric apparatus usually weighed between 0·8 and 1·2 g. Samples for the pressure measurement apparatus had weights within the range of 3–5 g. Blank values for the two systems were equivalent to 1·0–1·5 p.p.m. and about 3–4 p.p.m., respectively.

Discussion

Aspinal[3] has stated that a correction has to be applied to the mass 12 peak to account for the contribution from methane. The mass 15 peak is due to methane, this peak being used to calculate the methane contribution to the mass 12 peak, making use of the known cracking pattern of methane. This correction was determined at frequent intervals by the authors but was always found to be of the order of 0·1 to 0·3 p.p.m. of oxygen. Compared with the oxygen contents of the alloys this correction was negligible and was not applied.

The solubility of carbon in molten nickel baths is low, with a subsequent slow release of carbon monoxide. Therefore in the analysis of nickel-base alloys the samples should be interspersed among samples of steels or iron so as to ensure that the ratio of iron to nickel in the crucible is in excess of 3 to 1.

The results for the mass spectrometric determination of oxygen in ferrous and nickel-base alloys are considered to be satisfactory. However a recurrent problem was the heterogeneity of steels and other alloys with respect to oxygen concentration. Considerable scatter of analytical results was invariably found, owing to the difficulty of obtaining samples of identical composition. This would, of course, apply to all vacuum fusion systems, but the problem was somewhat more pronounced with the mass spectrometric equipment, due to the use of smaller samples. On the other hand, compared with conventional equipment, the mass spectrometric procedure involved less manipulation during a determination, for a gas separating system was unnecessary. Because the mass spectrometric equipment can be used to determine the oxygen contents of samples as small as 0·1 g., it should be particularly useful for determining the distribution of oxygen in a cross-section of material.

A comparison of the analytical performance of the two procedures is obtained from a study of the analytical results for the 2106 reference material. For this alloy, sixty oxygen determinations with the mass spectrometric equipment produced an average content of 39·5 p.p.m. with a standard deviation of 9·2 p.p.m. Sixty-four determinations using the transducer pressure measurement apparatus yielded a mean oxygen content of 39·0 p.p.m. with a standard deviation of 7·0 p.p.m. The slightly larger standard deviation with the mass spectrometric equipment is a result of the considerably smaller sample sizes. Of course, larger samples, leading to a lower standard deviation, could be used with a mass spectrometric apparatus too, if the sample lock were larger than the one in the authors' apparatus. This sample lock could not accommodate samples of weight in excess of 1·5 g.

In general the mass spectrometric results are in good agreement with the transducer results. Only with BES and TES samples (specification code HCM 3) were the transducer results slightly higher than the mass spectrometric results. On average this amounted to 3 p.p.m. It is felt that this might be due to the more extensive filing given to the mass spectrometric samples. For alloys of oxygen content less than 20 p.p.m., extra care should be taken to ensure that all oxide contamination is removed

TABLE II.—A COMPARISON OF THE RESULTS FOR THE DETERMINATION OF OXYGEN IN FERROUS METALS USING THE MASS SPECTROMETRIC FINISH AND THE TRANSDUCER PRESSURE MEASUREMENT FINISH

Sample	Average Oxygen Content (p.p.m.)*		Standard Deviation by Mass Spectrometry (p.p.m.)
	Transducer Pressure Measurement	Mass Spectrometry	
2106	39 (64)	40 (60)	9·2
B 1	9 (1)	9 (5)	2·0
B 2	—	12 (8)	2·7
B 3	5 (9)	7 (9)	1·2
B 4	—	11 (5)	2·9
Z 28	7 (12)	11 (9)	3·7
Z 29	11 (8)	9 (7)	2·2
Z 39	53 (2)	50 (6)	7·8
Z 50	15 (2)	18 (5)	2·9
VA 6976	10 (2)	11 (3)	—
VA 6977	11 (4)	9 (6)	1·6
VA 7866 (prep. in air)	—	7·1 (6)	0·3
VA 7866 (prep. in Ar)	—	7·3 (8)	1·3
BES 860 AB	17 (2)	11 (6)	0·9
BES 861 AB	20 (2)	14 (6)	2·2
BES 898 A	14 (2)	11 (10)	2·6
BES 899 A	17 (2)	14 (10)	0·6
BES 969 A	14 (2)	9 (4)	—
BES 971 A	19 (2)	16 (2)	—
BES 975 A	15 (2)	10 (4)	—
BES 977 A	9 (2)	9 (9)	1·1
BES 978 A	21 (2)	15 (6)	2·0
BES 979 A	18 (2)	16 (9)	0·6
BES 980 A	11 (2)	13 (9)	1·6
BES 981 A	13 (2)	12 (3)	—
BES 1079 A	16 (2)	11 (9)	1·0
BES 1080 A	11 (2)	9 (12)	0·9
TES 898 A3	18 (2)	18 (10)	2·2
TES 901 A1	17 (2)	13 (6)	2·1
TES 965 A	25 (2)	20 (6)	5·4
TES 980 A	17 (2)	23 (6)	2·1
TES 996 A3	17 (2)	17 (5)	0·7
TES 1079 A3	23 (2)	18 (12)	2·0
ZR 8/C	—	10 (5)	1·3
Specpure iron rod	—	38 (10)	5·5

*Figures in parenthesis refer to the number of determinations made on each sample.

from the surface with thorough filing. With alloy VA 7866, several samples were thoroughly filed in air and others in argon in a glove box before introduction to the sample arms of the furnace compartment. The average oxygen content of samples filed in air was within 1 p.p.m. of the average oxygen content of samples filed in argon (see Table I). Similar results were obtained with alloy B 4. For ferrous and nickel-base alloys of oxygen content between 4 and 20 p.p.m. a thorough filing in air followed by degreasing appears to be a satisfactory surface treatment before analysis.

The high sensitivity of the equipment was not fully realised, due to a lack of samples with a sufficiently low oxygen content and a lack of homegeneity within the alloy samples. The analytical data usually shows a standard deviation within the range of 0·6 to 2·5 p.p.m., a marked lack of homogeneity with respect to oxygen distribution being indicated by a standard deviation in excess of 3 p.p.m. The latent precision of the technique was partly approached with standard deviations in the region of 0·6 p.p.m., which were obtained with the most homogeneous materials. As operated, the mass spectrometric apparatus was more sensitive than the transducer equipment by a factor of approximately ten, and the sensitivity of the mass spectrometer could be further increased thirteenfold by use of a 300 μA. trap current in the instrument.

For oxygen determinations, the mass spectrometric finish is particularly recommended when only small weights of alloy are available for analysis and when the oxygen content is less than 10 p.p.m.

TABLE III.—A COMPARISON OF THE RESULTS FOR THE DETERMINATION OF OXYGEN IN NICKEL-BASE ALLOYS USING THE MASS SPECTROMETRIC FINISH AND THE TRANSDUCER PRESSURE MEASUREMENT FINISH

Sample	Average Oxygen Content (p.p.m.)*		Standard Deviation by Mass Spectrometry (p.p.m.)
	Transducer Pressure Measurement	Mass Spectrometry	
Z 31	15 (2)	17 (2)	—
Z 47	8 (2)	5 (5)	1·5
Z 48	7 (2	5 (11)	1·2
H 2589	5 (2)	15 (21)	7·2
EPK 24 (Rolls Royce)	4 (11)	7 (13)	2·3
Mintec A	—	12 (5)	7·1
Mintec B	—	13 (3)	—
Mintec C	—	8 (4)	—
Mintec D	—	6 (3)	—
Mintec E	—	7 (6)	2·2
Mintec F	—	4 (2)	—
Mintec G	—	6 (3)	—
Mintec H	—	7 (4)	—

*Figures in parenthesis refer to the number of determinations made on each sample.

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THE DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN FERROMOLYBDENUM

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Molybdenum in ferromolybdenum has frequently been determined gravimetrically after precipitation as lead molybdate, but this method is tedious since a double precipitation of the molybdenum is required. Since ferromolybdenum consists mainly of molybdenum and iron with minor or trace amounts of carbon, silicon, phosphorus, sulphur, copper and perhaps other elements, it seemed possible that a differential spectrophotometric method could be developed for the determination of molybdenum in the alloy. For such a method it is desirable to use alloy samples with weights in the range 0.5–1 g, which corresponds to weights of molybdenum between 0.2 and 0.8 g; accordingly, the coloured compound used in the differential method must not have a high molar absorptivity. The simple compounds of the transition elements frequently have molar absorptivities between 1 and 200 and have been used in differential spectrophotometric methods. For example, Bastian[1] has used this technique to determine copper in copper-base alloys, and Bacon and Milner[2] have applied it to uranium in uranium metal and in triuranium octoxide.

Simple molybdenum(VI) compounds are generally colourless but simple molybdenum(V) compounds are coloured with low molar absorptivities and are readily produced from molybdenum(VI) on reaction with mild reducing agents.

A method for the differential spectrophotometric determination of molybdenum in solutions of ferromolybdenums after the reduction of molybdenum(VI) to molybdenum(V) and of iron(III) to almost colourless iron(II) is reported in this paper.

Preliminary investigations

Molybdenum(VI) in dilute hydrochloric acid is conveniently and quantitatively reduced to molybdenum(V) with an excess of hydrazine sulphate[3]. It was verified that molybdenum(VI) is, in fact, reduced to reddish-orange molybdenum(V) by hydrazine sulphate in 1.2 *M* hydrochloric acid on heating at 95° for 10 min. However, in this medium, iron(III) was not completely reduced to iron(II); a yellowish-green colour remained in a solution containing only iron after this treatment. When an excess of sodium sulphite solution was added to this yellowish-green solution, such that the hydrochloric acid concentration was *ca.* 0.13 *M*, and when the solution was heated to 95° for 10 min, the iron(III) was reduced to almost colourless iron(II). However, if this final hydrochloric acid concentration of *ca.* 0.13 *M* was exceeded, complete reduction of iron(III) to iron(II) did not appear to be achieved. Unfortunately, when this reduction treatment was applied to solutions of ferromolybdenums, a bluish-black colour was produced after adding hydrazine sulphate and heating (hydrochloric acid

concentration 1.2 *M*). This colour was probably due to molybdenum blue or heteropoly blues formed in the dilute acid solutions; it should not be formed in more concentrated hydrochloric acid solutions but these were not compatible with complete reduction of iron(III).

Therefore, sulphuric acid media were examined. In sulphuric acid, molybdenum(VI) and iron(III) are reduced to molybdenum(V) and iron(II), respectively, by heating at 95° first with an excess of hydrazine sulphate and then with an excess of sodium sulphite. At the molybdenum reduction stage, the concentration of sulphuric acid in the solution was *ca.* 2.3 *M* and at the iron reduction stage, *ca.* 1.2 *M*. The final solution was reddish-orange in colour. Samples of ferromolybdenums reacted in a similar way to give clear reddish-orange solutions. These solutions showed a broad peak in the absorption spectrum with a maximum at 390 nm.

EXPERIMENTAL

Apparatus

A Hilger and Watts Uvispek Spectrophotometer was used for the differential spectrophotometry with accurately matched quartz cells of 1 cm light path.

Teflon beakers (150 ml) and covers (XIon Products, London) were used. Grade A volumetric glassware was used.

Reagents

Molybdenum sheet, either high-purity (Murex) or 99.9% (Koch-Light), and iron powder ("Specpure", Johnson and Matthey, London) were used. Nitric acid (d. 1.42), sulphuric acid (98% w/w) and hydrofluoric acid (40% w/w) were of analytical-reagent grade.

Copper sulphate solution (6 *mg Cu* ml^{-1}). Dissolve 2.358 g of A.R. copper sulphate pentahydrate in 100 ml of solution.

Orthophosphoric acid solution (6 *mg P* ml^{-1}). Dissolve 1.23 ml of A.R. orthophosphoric acid (d. 1.75) in 100 ml of solution.

Other stock solutions of metal ions for interfering effects were prepared from high purity metals or from salts of A.R. quality.

Procedure

To 0.6000 g of ferromolybdenum, accurately weighed, in a Teflon beaker add 5 ml of sulphuric acid (1+2). Carefully add in small portions, 3 ml of concentrated nitric acid, followed by 2 ml of concentrated hydrofluoric acid (Note 1). Heat the beaker on a hot plate at a low temperature and then increase the temperature gradually until white fumes of sulphur trioxide are evolved. Continue the fuming for a further 10 min. Cool the solution. A small yellow residue remains. Carefully add 15 ml of distilled water and then 4 ml of concentrated sulphuric acid gradually (Note 2). The precipitate usually dissolves, but if it does not, warm the beaker until a clear yellow solution is obtained. Add 20 ml of 3% (w/v) hydrazine sulphate solution and heat to *ca.* 95° for about 15 min. The reduction of molybdenum(VI) to molybdenum(V) occurs at this stage, and the solution gradually becomes reddish-orange. Cool the beaker and contents, add 20 ml of 1 *M* sodium sulphite solution and heat again at *ca.* 95° for about 20 min. The iron(III) is reduced to iron(II). Cool the solution, transfer it

to a 100-ml graduated flask, and make up almost to the mark with distilled water.

At the same time, prepare in a similar way six standard solutions of molybdenum plus iron containing a total of exactly 0.6 g of these elements. The most dilute molybdenum solution should contain less molybdenum than that in the sample solution. If the most dilute molybdenum solution corresponds to x% molybdenum in a ferromolybdenum then the other solutions should correspond to $(x+2)$ %, $(x+4)$ %, $(x+6)$ %, $(x+8)$ % and $(x+10)$ % of molybdenum. The sample(s) for analysis should contain more than x% of molybdenum but less than $(x+10)$ % of this element.

When all solutions have attained room temperature, make up to the mark with distilled water.

Select a wavelength of 390 nm. Add the most dilute standard molybdenum solution to one cell (Note 3) and a more concentrated molybdenum solution (a standard or a sample solution) to the other cell. Place the more dilute solution in the light path and set 0% transmission with the shutter in position. Remove the shutter and set 100% transmission by appropriate operation of the slit width and check controls. Place the other molybdenum solution in the light path and measure its absorbance. Repeat this procedure for all the standard and sample solutions (Note 4). Draw up a calibration graph for the standard solutions in the usual way and read off the concentration of molybdenum in the ferromolybdenum(s).

Note 1. Silicon should be removed as volatile silicon tetrafluoride. Otherwise a cloudiness due to silica is obtained in the final solution.

Note 2. When the solution is heated to fumes, only *ca.* 1 ml of sulphuric acid remains. It was found preferable in later work to add the 4 ml of concentrated sulphuric acid immediately after the hydrofluoric acid, before the fuming stage (see p. 218).

Note 3. The cells were cleaned by rinsing them in turn with acetone, benzene, concentrated sulphuric acid and finally distilled water. They were, of course rinsed with the appropriate solution before use.

Note 4. The absorbances of solutions measured differentially were constant for two days.

Tests for interfering elements

Phosphorus. Nine synthetic solutions were prepared each corresponding to 600-mg samples of ferromolybdenum containing 70% molybdenum, 30% iron, and 0, 0.03, 0.04, 0.05, 0.08, 0.10, 0.15, 0.20 and 0.25% of phosphorus. These solutions were analysed as described above. The absorbances of the molybdenum(V) solutions were measured against a standard solution containing 370 mg of molybdenum plus 230 mg of iron carried through a similar procedure. The percentage of molybdenum in each case was read from a calibration graph. Figure 1, curve A, shows the apparent molybdenum content of these 600-mg samples of simulated ferromolybdenums containing the different concentrations of phosphorus. There is no interference effect for 0.03% or less of phosphorus.

Copper. A similar graph is shown in Figure 1 (curve B) for simulated ferromolybdenums containing 70% of molybdenum and 0, 0.25, 0.5, 0.75 and 1.5% of copper. A black precipitate was also obtained in solutions containing copper at concentrations equivalent to or greater than 0.5% of copper in a ferromolybdenum.

Other elements. Similar studies were made with other elements. There were no interfering effects on the determination of molybdenum in simulated ferromolyb-

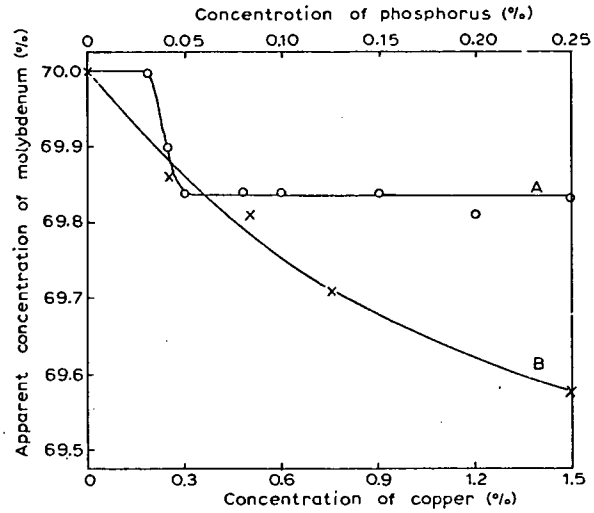

Fig. 1. The effect of low concentrations of phosphorus (curve A) and copper (curve B) on the differential spectrophotometric determination of molybdenum in simulated ferromolybdenums. All solutions contained the equivalent of 70.00% of molybdenum.

denums containing 70% of molybdenum, from 0.2% of arsenic, from 0.5% of lead, antimony, bismuth, tungsten, manganese, nickel and zinc, and from 3% of aluminium.

RESULTS FOR A SERIES OF FERROMOLYBDENUMS

The above method was applied to the analysis of fourteen ferromolybdenums; the results are shown in Table I (the first fourteen results).

Alloy No. 13 was analysed twelve times to establish the precision of the method. The average molybdenum content was found to be 75.32% with a standard deviation of 0.08% and a relative standard deviation of 0.11%.

When the investigation was nearing completion, it was realized that a slight improvement on the initial method was possible. In the initial method, on heating to fumes of sulphur trioxide, very little sulphuric acid remained in the beaker. Therefore it seemed better to add all of the sulphuric acid before fuming, for then *ca.* 5 ml of sulphuric acid was present in the beaker at the fuming stage (see Note 2). This slight amendment to the method would not affect the results for the first fourteen alloys in Table I. This was verified by analysing alloys Nos. 10 and 12 by the amended method. Results for the molybdenum contents of alloys 10 and 12 were 72.80% and 72.76%, and 75.20% and 75.26%, respectively. The average results of 72.78% and 75.23% are in close agreement with the values given for these alloys in Table I. Two further alloys (15 and 16) were analysed by the amended method and their molybdenum contents are also given in Table I.

DISCUSSION

The precision of the results obtained by the described method (Table I) is good but the average results are usually slightly low compared with the results given by the

TABLE I

RESULTS FOR THE DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN FERROMOLYBDENUMS

Alloy number	*Mo content* (%)[a]	*Mo content found*		*Difference Col. 4 – Col. 2* (%)	*Corrected Mo content* (%)[b]	*Difference Col. 6 – Col. 2* (%)
		Individual results (%)	*Average* (%)			
1	46.5	46.30, 46.40, 46.41	46.37	−0.1	46.4	−0.1
2	48.6	48.33, 48.50, 48.41	48.41	−0.2	48.5	−0.1
3	60.9	60.95, 60.90, 61.05	60.97	+0.1	70.0	+0.1
4	68.9	69.00, 69.10, 68.75	68.95	+0.1	69.1	+0.2
5	70.03	69.91, 69.70, 69.93	69.85	−0.2	70.0	0
6	70.5	70.23, 70.33	70.28	−0.2	70.3	−0.2
7	71.41	71.33, 71.30	71.32	−0.1	71.4	0
8	71.9	71.79, 71.79	71.79	−0.1	71.9	0
9	72.46	72.40, 72.25, 72.45	72.37	−0.1	72.5	0
10	72.9	72.70, 72.75	72.73	−0.2	72.8	−0.1
11	72.98	72.88, 72.86	72.87	−0.1	73.0	0
12	75.3	75.10, 75.20	75.15	−0.2	75.3	0
13	75.40	75.35, 75.30, 75.41	75.35	0	75.5	+0.1
BCS 231/4	70.0	69.50, 69.60	69.55	−0.4	69.8	−0.2
15	69.10	68.67, 68.69	68.68	−0.4	68.9	−0.2
16	71.00	70.69, 70.85	70.77	−0.2	70.8	−0.2

[a] Determined by the supplier.
[b] See p. 218.

supplier. Ferromolybdenum seldom contains more than 0.05% of phosphorus and this could account for no more than 0.2% of the negative bias (see Fig. 1, curve A). However, the molybdenum content for BCS 231/4 determined by the described method was 0.4% low and it was interesting that a black precipitate was formed in the alloy solution on heating after the addition of sodium sulphite solution. Spectrographic analysis of the precipitate showed that it contained copper, and wet chemical analysis that it also contained sulphide. As reported earlier, a similar precipitate was

TABLE II

RESULTS FOR THE DETERMINATION OF COPPER IN FERROMOLYBDENUMS

Alloy	1	2	3	4	5	6	7	8
Copper content (%)	0.07	0.26	0.06	0.18	0.14	0.05	0.22	0.19
Alloy	9	10	11	12	13	BCS 231/4	15	16
Copper content (%)	0.22	0.14	0.27	0.11	0.22	0.55	0.53	0.10

obtained for simulated ferromolybdenums containing more than 0.5% of copper. Therefore, it seemed likely that at least part of the negative bias might be due to the alloy samples containing copper.

The ferromolybdenums were analysed for copper content by conventional atomic absorption spectroscopy, with the results shown in Table II.

Corrections could be applied to the molybdenum figures in Table I for the copper contents of these alloys based on Fig. 1, curve B. When this was done the

corrected results shown in Table I were obtained. The average negative bias was then −0.04%, which could be explained by the presence of trace amounts of phosphorus in these alloys. The results are considered to be good.

A satisfactory method has, therefore, been developed for the differential spectrophotometric determination of molybdenum in ferromolybdenums of low copper and phosphorus content. If a reducing agent other than sulphite can be found for the reduction of iron(III), the slight interference from copper should be eliminated. It is felt that sulphur dioxide and hydrazinium ions must have reacted to produce a little hydrogen sulphide which brought about precipitation of a small amount of copper sulphide. This precipitate could carry down small amounts of molybdenum and result in a slight lowering in the absorbance of the solution containing molybdenum(V).

We are indebted to High Speed Steel Alloys Ltd., London and Scandinavian Metallurgical Co. Ltd., Minworth Metals Ltd. and Murex Ltd. for supplying analysed samples of ferromolybdenum and to Murex Ltd. for a gift of high-purity molybdenum sheet.

SUMMARY

A differential spectrophotometric method is described for the determination of molybdenum in ferromolybdenums based on the reddish-orange molybdenum(V) species formed in sulphuric acid solution on reduction with hydrazine sulphate. Interference from iron is eliminated by reduction of the iron(III) to iron(II) with sulphur dioxide. Of the elements that could be found in minor or trace amounts in ferromolybdenum, only copper and phosphorus show slight interfering effects. When account was taken of the slight interference from copper in the determination of molybdenum in sixteen ferromolybdenums, results of good accuracy and precision were obtained.

RÉSUMÉ

On décrit une méthode spectrophotométrique différentielle pour le dosage du molybdène dans des ferromolybdènes, basée sur la formation de composés de molybdène(V) orange rouge, formés en milieu acide sulfurique par réduction à l'aide de sulfate d'hydrazine. L'interférence du fer est éliminée par réduction en fer(II) au moyen d'anhydride sulfureux. Parmi les éléments pouvant se trouver à l'état de traces dans un ferromolybdène, seuls le cuivre et le phosphore présentent une légère interférence.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Differentialmethode beschrieben für die Bestimmung von Molybdän in Ferromolybdän-Proben. Sie beruht auf der Bildung von rötlich-orangefarbenen Molybdän(V)-Spezies in schwefelsaurer Lösung nach Reduktion mit Hydrazinsulfat. Die Störung durch Eisen wird durch Reduktion von Eisen(III) zu Eisen(II) mit Schwefeldioxid beseitigt. Von den Elementen, die in Ferromolybdän in geringen Mengen oder als Spuren vorkommen, stören nur Kupfer und Phosphor etwas. Durch Berücksichtigung der geringen Störung durch Kupfer bei der Bestimmung von Molybdän in sechzehn Ferromolybdän-Proben wurden Ergebnisse von guter Genauigkeit und Reproduzierbarkeit erhalten.

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Section 6. List of publications

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APPENDIX 2

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APPENDIX 3

Organisations who have supported or are supporting the work of the author

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Steel Castings Research and Trade Association

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